PB88-154299

Acidic Episodes and Surface Water Chemistry A Comparison of Northeast and Southeast Study Sites

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Prepared for

Corvallis Environmental Research Lab., OR

May 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB88-154299

EPA/600/3-87/018
May 1987

ACIDIC EPISODES AND SURFACE WATER CHEMISTRY: A COMPARISON OF NORTHEAST AND SOUTHEAST STUDY SITES

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REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/3-87/018

2.

3. RECIPIENT'S ACCESSION NO.
PB88 154299/AS

4. TITLE AND SUBTITLE
ACIDIC EPISODES AND SURFACE WATER CHEMISTRY: A Comparison of Northeast and Southeast Study Sites

5. REPORT DATE
May 1987

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
*Baptist University. Arkadelphia, AR
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10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
CR811863

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Research Laboratory, US EPA
Office of Research & Development
Corvallis, OR 97333

13. TYPE OF REPORT AND PERIOD COVERED
Project Report

14. SPONSORING AGENCY CODE
EPA 600/02

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Much of the emphasis in the National Acid Precipitation Assessment Program (NAPAP) has been on historical or longterm trends in surface water acidification. Short-term acidic episodes, however, also might have significant adverse effects on aquatic ecosystems. The U.S. EPA is presently designing an Episodic Response Project to investigate the regional extent, frequency, duration and magnitude of acidic episodes. The studies discussed in this report, however, were conducted under NAPAP Task Group E2-Aquatic Effects. A total of four episodic studies were conducted in the Catskill Mountains of New York (Murdoch, USGS), Laurel Hills, PA (Witt and Barker, USGS), Southern Blue Ridge Province, NC, TN (Olem, TVA), and Ouachita Mountains, AR (Nix et al., Ouachita Baptist University). The purpose of this report is to integrate major aspects of these four studies in a single document.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
Release to the Public

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
166

22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

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PREFACE

Much of the emphasis in the National Acid Precipitation Assessment Program (NAPAP) has been on historical or long-term trends in surface water acidification. Short-term acidic episodes, however, also might have significant adverse effects on aquatic ecosystems. The U.S. EPA is presently designing an Episodic Response Project to investigate the regional extent, frequency, duration and magnitude of acidic episodes. The studies discussed in this report, however, were conducted under NAPAP Task Group E2-Aquatic Effects. A total of four episodic studies were conducted in the Catskill Mountains of New York (Murdoch, USGS), Laurel Hills, PA (Witt and Barker, USGS), Southern Blue Ridge Province, NC, TN (Olem, TVA), and Ouachita Mountains, AR (Nix et al., Ouachita Baptist University). The purpose of this report is to integrate major aspects of these four studies in a single document.

SIGNIFICANT FACTS

During part of 1984 and 1985, four studies were conducted in the northeastern and southeastern regions of the United States to investigate the effects of acidic episodes on stream chemistry. Significant facts based upon integrating the results from these studies are:

- Each of the streams studied was typical of streams in the geographic regions in which they were located. Each stream maintained continuous streamflow throughout the year and supported a sport fishery.

- Acidic deposition ($pH < 5.0$) occurred at all sites.

- pH and acid neutralizing capability (ANC) decreased during storm events at all sites. pH depressions of 0.5 - 1.3 units were noted in about 55 percent of the storms (i.e., 31 storms).

- Assuming our estimates for dry deposition are reasonable, the northeastern sites were in steady state with respect to sulfate inputs and outputs.

- Minimum pH and ANC values generally were lower during events in the northeastern sites, which were near steady state with respect to sulfate, than in the southeastern sites, which were retaining sulfate.

- Biscuit Brook, in the Catskill Mountains, NY, and South Fork Bens Creek, in the Laurel Hills, PA, were near steady state with respect to nitrate during the 1984 budget period, (i.e. About 11-14 percent nitrate retention).

- Episodes of alkalinity and pH depressions can occur at any time of the year, but the probability of occurrence is greater during snowmelt and periods when watershed soils are saturated.

- Developing a protocol and procedures for estimating the probability that episodes will occur is feasible.

EXECUTIVE SUMMARY

There is a growing awareness that super-imposed on long-term acidification of surface waters are short-term acidic episodes where rapid depressions of pH and ANC occur within hours or days. Four studies were conducted during part of 1984 and 1985 to investigate the effects of acidic episodes on stream chemistry. This report integrates the results of the four studies to identify commonalities and differences among the study sites.

The study sites (regions) and principal investigators were:

Study Area	Principal Investigator
Biscuit Brook, NY (Catskill Mountains)	Pete S. Murdoch, USGS
North and South Fork Bens Creeks, PA (Laurel Hills)	Emitt C. Witt and James L. Barker, USGS
Moses and Jarrett Creeks, NC (Southern Blue Ridge Province)	Harvey Olem, TVA
East Fork Saline River, AR (Ouachita Mountains)	Joe F. Nix and Kent W. Thornton, Ouachita Baptist University

To ensure comparability of results, methodology was standardized among sites. Each investigator monitored baseflow chemistry and attempted to sample nine storm, including snowmelt, events throughout the year. Analytical methods were similar to those used in the National Surface Water Survey (NSWS) (Hillman et al. 1986).

Based on physiographic characteristics and forest cover, the sites were similar to each other and each was probably typical of the region in which it was located. All sites receive acidic deposition.

Analyses of the results showed that episodes (i.e., decreases in acid neutralizing capability (ANC)) occurred at all sites during all seasons. Acidic episodes (i.e., an episode with a ANC < 0.0 ueq/l) were observed at Biscuit Brook on 13 December 1983 (-12.0 ueq/l), on 5-6 April 1984 (-0.80 to -12 ueq/l) and on 27-28 September 1985 (-8.0 and -14.0 ueq/l). Both the North and South Fork Bens Creeks experienced episodes where the pH dropped to about 5.20 or less, roughly equivalent to an ANC of 0 ueq/l. The East Fork Saline River experienced one event that had a minimum ANC of 0.4 ueq/l (December, 1985). The magnitude and duration of these monitored events, however, varied among and within sites.

Snowmelt events were observed at the Biscuit Brook and North Fork Bens Creek sites. Aluminum and nitrate concentrations increased during the snowmelt events. In two of the three snowmelt events there were no apparent relationships between sulfate and pH or sulfate and discharge. During the 11-13 March 1985 event at Biscuit Brook, sulfate concentrations decreased with increased discharge with minimum sulfate concentration coinciding with the peak of the hydrograph. At the Biscuit Brook site, ANC concentrations decreased dramatically during the snowmelt event.

During the storm event (i.e., rainfall) pH and ANC decreased and aluminum increased at all sites. Sulfate concentrations generally decreased during storm events at Biscuit Brook, but increased slightly or remained relatively constant at the other sites.

Annual mass budgets were calculated for water, hydrogen ions, nitrate, sulfate, sum of anions, and sum of cations at the study sites. Hydrogen was being retained by all watersheds and anions and base cations were being exported. The watersheds of Biscuit Brook and South Fork Bens Creek exported sulfate, whereas the watersheds of Moses Creek, Jarrett Creek, and the East Fork Saline retained sulfate. Nitrate was near steady state at the Biscuit Brook and South Fork Bens Creek sites for the 1984 budget period (i.e. About 11-14 percent nitrate retention). Greater than 90% of the nitrate was retained in Jarrett Creek, Moses Creek, and the East Fork Saline River.

The number of sites and the study duration precluded the identification of specific regional patterns or criteria for delineating episodes but did permit the following conclusions:

- Each of the streams studied was typical of streams in the geographic regions in which they were located. Each stream maintained continuous streamflow throughout the year and supported a sport fishery.

- Acidic deposition ($pH < 5.0$) occurred at all sites.

- pH and acid neutralizing capability (ANC) decreased during storm events at all sites. pH depressions of 0.5 - 1.3 units were noted in about 55 percent of the storms (i.e., 31 storms).

- Assuming our estimates for dry deposition are reasonable, the northeastern sites were in steady state with respect to sulfate inputs and outputs.

- Minimum pH and ANC values generally were lower during events in the northeastern sites, which were near steady state with respect to sulfate, than in the southeastern sites, which were retaining sulfate.

- Biscuit Brook, in the Catskill Mountains, NY, and South Fork Bens Creek, in the Laurel Hills, PA, were near steady state with respect to nitrate during the 1984 budget period, (i.e. About 11-14 percent nitrate retention).

- Episodes of alkalinity and pH depressions can occur at any time of the year but the probability of occurrence is greater during snowmelt and periods when the watershed soils are saturated.

- Developing a protocol and procedures for estimating the probability that episodes will occur is feasible.

DEFINITIONS

The following definitions are used throughout this report.

Acid Neutralizing Capacity

Acid neutralizing capacity (ANC) is the capacity of a solution to neutralize acidic inputs. ANC is operationally defined as the equivalent sum of all the bases that can be titrated with a strong acid to a preselected equivalence point or reference level (Stumm and Morgan 1981). In a bicarbonate dominated system, ANC and alkalinity (see Alkalinity definition) are roughly equivalent. In dilute surface waters such as often studied in relation to acidification, however, total inorganic carbon concentrations are low and therefore ANC due to the carbonate system is low. In these dilute systems, other species such as naturally formed weak organic acids, (when dissociated) and aluminum-hydroxy compounds leached from soils and sediments can contribute measurably to ANC (Church 1983).

Acidic

An acidic system is defined as a system with ANC < 0.0 ueq/l. Because the pH at the equivalence point is dependent on the initial inorganic carbon concentration this can correspond to pH values from 5.0 to about 5.6.

Acidification

Acidification is defined as the loss of acid neutralizing capacity (Galloway 1984). Acidic systems and acidification can result from both naturally and/or anthropogenically derived acids. Unless specifically stated, no inferences about natural versus anthropogenic sources are implied when using the terms acidic or acidification in this report.

Alkalinity

Alkalinity is a measure of the capacity of an aqueous solution to neutralize acid (Church 1983). In carbonate dominated systems and many natural waters, acid neutralizing capacity (ANC) is often referred to as alkalinity (Stumm and Morgan 1981) because ANC and alkalinity are roughly equivalent. Bicarbonate represents the major form of alkalinity and is formed from the action of carbon dioxide upon basic materials in the soil. Alkalinity does not include the salts of other weak acids, such as organic acids that might be present in small amounts.

Buffering Capacity

Buffering capacity is the ability of an aqueous solution to resist change in pH with the addition of an acid or base (Stumm and Morgan 1981).

Duration

For purposes of this document, the duration of an event was defined as the time between the beginning and end of the event. The beginning of the event occurred when the hydrograph started to rise or when data collection began, if it commenced after the rise in the hydrograph began. The end of the event occurred when flow and water quality returned to pre-event levels or when data collection stopped.

Event

A hydrologic event refers to a distinct period of increased water flow (discharge) or runoff resulting from rainfall and/or snowmelt. For purposes of this document two criteria were used to define an event:

1) there was a definite rise and fall in the hydrograph; and

2) there were adequate data to characterize the constituents during the rise and fall of the hydrograph.

Episodes

Episodes occur when acidification takes place during a hydrologic event. Episodes are therefore considered to be a subset of hydrometeorological events, and can occur in response to either rainfall or snowmelt.

TABLE OF CONTENTS

1.0 INTRODUCTION.. 1-1
  1.1 Historical Perspective and Acidic Deposition..1-1
  1.2 Problem Definition............................1-2
    1.2.1 Snowmelt Episodes.......................1-3
    1.2.2 Stormflow Episodes......................1-5
  1.3 Site Comparisons..............................1-6

2.0 STUDY AREAS 2-1
  2.1 Physiographic Features........................2-1
  2.2 Hydrometeorology..............................2-6
  2.3 Land Use.....................................2-10
  2.4 Geology......................................2-13
  2.5 Soils 2-15
  2.6 Regional Quality Patterns of Precipitation...2-19
  2.7 Fish Resources...............................2-19

3.0 METHODOLOGY 3-1
  3.1 Wet Deposition................................3-1
  3.2 Flow Measurements.............................3-3
  3.3 Stream Chemistry 3-3
  3.4 Laboratory Analysis and Quality Control.......3-5
  3.5 Mass Budgets..................................3-8

4.0 RESULTS 4-1
  4.1 Water Budgets.................................4-1
  4.2 Wet Deposition Chemistry......................4-2
    4.2.1 Composition.............................4-3
    4.2.2 Spatial (Regional) Variability..........4-9
    4.2.3 Seasonal Variability...................4-10
  4.3 Baseflow Stream Chemistry....................4-12
    4.3.1 Site Variation (Annual)................4-19
      4.3.1.1 pH.................................4-19
      4.3.1.2 Base Cations.......................4-19
      4.3.1.3 ANC and Anions.....................4-19
      4.3.1.4 Dissolved Aluminum.................4-20
    4.3.2 Seasonal Variability...................4-20
      4.3.2.1 pH.................................4-20
      4.3.2.2 Base Cations.......................4-20
      4.3.2.3 ANC and Anions.....................4-27
      4.3.2.4 Dissolved Aluminum.................4-27
      4.3.2.5 Comparison.........................4-28
  4.4 Episodes.....................................4-28
    4.4.1 Snowmelt Episodes......................4-30
    4.4.2 Storm Episodes.........................4-38
    4.4.3 Mean Episode Chemistry.................4-48
      4.4.3.1 pH.................................4-48
      4.4.3.2 Base Cations.......................4-51
      4.4.3.3 ANC and Anions.....................4-51
      4.4.3.4 Dissolved Aluminum.................4-51

4.5 Mass Budgets....................................4-51
  4.5.1 Water Budget..........................4-54
  4.5.2 Hydrogen 4-54
  4.5.3 Sulfate 4-54
  4.5.4 Nitrate 4-54

5.0 DISCUSSION 5-1
  5.1 Study Sites......................................5-2
  5.2 Deposition Chemistry.........................5-3
  5.3 Watershed Response............................5-6
    5.3.1 Canopy Interactions.....................5-6
    5.3.2 Geology.................................5-10
    5.3.3 Soil Interaction........................5-10
  5.4 Stream Response................................5-13
  5.5 Biological Effects.............................5-15
  5.6 Budgets..5-16
  5.7 Frequency of Episodes.........................5-22
  5.8 Discharge-Concentration Relations............5-24
  5.9 Limitations......................................5-29

6.0 SUMMARY AND CONCLUSIONS.............................6-1

7.0 REFERENCES 7-1

APPENDIX A: Stage-Discharge Calculations:
Jarrett and Moses Creeks...................A-1
APPENDIX B: National Atmospheric Deposition
Program/National Trends Network Monitoring
Stations Used to Determine Regional
Constituent Concentrations.................B-1

LIST OF TABLES

Table 2.1 Comparison of physiographic characteristics....................2-2
Table 2.2 Comparison of climatology....................2-7
Table 3.1 Precipitation quantity and quality sampling intervals....................3-2
Table 3.2 Sampling procedures for stream chemistry at each site....................3-4
Table 3.3 Water quality variables measured at each site....................3-6
Table 4.1 Comparison of site and regional wet deposition components....................4-4
Table 4.2 Seasonal trends in wet deposition composition....................4-6
Table 4.3 Annual flow-weighted streamflow composition 4-13
Table 4.4 Flow-weighted seasonal streamflow composition for Biscuit Brook (Oct 83 - Sep 84)....................4-21
Table 4.5 Flow-weighted seasonal streamflow composition for South Fork Bens Creek (Oct 83 - Sep 84)....................4-22
Table 4.6 Flow-weighted seasonal streamflow composition for North Fork Bens Creek (Oct 83 - Sep 84)....................4-23
Table 4.7 Flow-weighted seasonal streamflow composition for Jarrett Creek (May 84 - Mar 85)....................4-24
Table 4.8 Flow-weighted seasonal streamflow composition for Moses Creek (May 84 - Mar 85)....................4-25
Table 4.9 Flow-weighted seasonal streamflow composition for East Fork Saline (Nov 84 - Oct 85)....................4-26
Table 4.10 Seasonal trends in stream chemistry.........4-29
Table 4.11 Summary of episodes....................4-31
Table 4.12 Relative change in concentration of stream constituents during episodes.........4-46
Table 4.13 Comparison of mean event and mean annual baseflow concentrations (all units are ueq/l except pH which is s.u. and aluminum which is ug/l)....................4-49
Table 4.14 Annual mass budgets....................4-52
Table 5.1 Average annual sulfate input-output budgets (SO_4-S) for sites in the U.S. and Canada (kg $ha^{-1}yr.^{-1}$) (Rochelle et al. 1986)......5-18
Table 5.2 Relation of site study year precipitation to historical precipitation................5-31

LIST OF FIGURES

Figure 1.1 Location of the four study areas............1-7
Figure 2.1 Photographs of the study sites..............2-3
Figure 2.2 Regional average monthly precipitation and runoff for the four study sites.........2-9
Figure 2.3 Representative annual hydrographs for the four study regions.....................2-11
Figure 2.4 General soil classification for the Northeast and Southeast (modified from McFee 1980)..........................2-16
Figure 2.5 Wet deposition pH isopleths for 1980-82 (Modified from 1983 Annual NAPAP Report)...2-20
Figure 2.6 1980 weighted average sulfate ion concentrations (ueq/l) for wet deposition samples. (Adapted from Barrie et al. 1982)........................2-21
Figure 2.7 Total alkalinity map of the Eastern United States (after Omernik et al. 1986)..................................2-22
Figure 4.1 Volume-weighted average precipitation chemistry for the study period..............4-7
Figure 4.2 Volume-weighted average precipitation chemistry by season.........................4-8
Figure 4.3 Flow-weighted average stream chemistry for the study period.......................4-14
Figure 4.4 Flow-weighted average stream chemistry for the winter period......................4-15
Figure 4.5 Flow-weighted average stream chemistry for the spring period......................4-16
Figure 4.6 Flow-weighted average stream chemistry for the summer period......................4-17
Figure 4.7 Flow-weighted average stream chemistry for the fall period........................4-18
Figure 4.8 Selected variables from a snowmelt event on Biscuit Brook, NY - February 1985.......4-34
Figure 4.9 Selected variables from a snowmelt event on Biscuit Brook, NY - March 1985..........4-35
Figure 4.10 Selected variables from a snowmelt event on North Fork Bens Creek, PA - 1985........4-36
Figure 4.11 Selected variables from a storm event on Biscuit Brook, NY - 1983................4-39
Figure 4.12 Selected variables from a storm event on South Fork Bens Creek, PA - 1984........4-40
Figure 4.13 Selected variables from a storm event on Jarrett Creek, NC - 1985................4-41
Figure 4.14 Selected variables from a storm event on Moses Creek, NC - 1984..................4-42
Figure 4.15 Selected variables from a storm event on East Fork Saline River, AR - 1984.......4-43
Figure 4.16 Selected variables from a storm event on East Fork Saline River, AR - 1985.......4-44

LIST OF FIGURES (Continued)

Figure 4.17 Mean event stream chemistry concentrations............................4-50
Figure 5.1 Average number of days of thunderstorms per year (after Geraghty et al. 1973)...........5-5
Figure 5.2 Comparison of precipitation and throughfall pH in the East Fork Saline River, AR........5-7
Figure 5.3 Comparison of precipitation and throughfall ANC in the East Fork Saline River, AR.......5-8
Figure 5.4 Percent sulfate retention for the intensively studied sites in the U.S. and Canada relative to the southern extent of Wisconsinan glaciation (Rochelle et al. 1986)..........5-21
Figure 5.5 Hysteresis in discharge - sodium concentrations, East Fork Saline River, 10-13 December 1985........................5-26
Figure 5.6 Stream pH values observed at two stations of comparable watershed size (North Fork and Campsite) and one station with a larger watershed (East Fork)......................5-27
Figure 5.7 Stream ANC values observed at two stations of comparable watershed size (North Fork and Campsite) and one station with a larger watershed (East Fork)......................5-28

ACIDIC EPISODES AND SURFACE WATER CHEMISTRY: A COMPARISON OF NORTHEAST AND SOUTHEAST STUDY SITES

1.0 INTRODUCTION

1.1 HISTORICAL PERSPECTIVE AND ACIDIC DEPOSITION

The extent, potential causes, consequences and corrective actions for surface water acidification have received extensive study and attention during the last decade (Drablos and Tollan 1980, NAS 1981, NRCC 1981, Altshuller and Linthurst 1984). Acidic deposition has resulted in the acidification of lakes and streams and the loss of fisheries resources in some acidic systems (Baker 1984, Schofield 1976, Schofield and Trojnor 1980, Wright 1977). Surface water acidification is neither new nor caused solely by anthropogenic inputs (Hutchinson 1957, Patrick et al. 1981). Naturally acidic lakes and streams can occur as the result of a variety of natural processes, such as geothermal activity and organic acid leaching (Magnuson and Rahel 1983); processes occurring long before anthropogenic emissions contributed to atmospheric acidity.

The current concern over freshwater acidification occurs because, in some geographic locations, acidic inputs are at levels greater than some watersheds and aquatic systems can assimilate. For the biota in these systems, the rate of change of surface water chemistry might be more significant than the tendency toward decreased pH.

To understand the effects of acidic deposition requires an understanding both of the dynamic processes involved in neutralizing acidic inputs by the watershed and aquatic environments and the rates at which these processes take place. For example, neutralization of acidic deposition in a watershed is ultimately determined by the rate at which weathering reactions (dissolution) in geologic materials occurs (Johnson 1984). Surface water chemistry is also influenced by the rate at which water moves through various soil horizons and the rates at which chemical reactions (e.g., cation exchange, sulfate adsorption/desorption) and biological processes (e.g., denitrification) occur as the water moves through the watershed.

Historically, acidification of Norwegian streams during spring melt and the attendant fish kills were largely responsible for initiating research that lead to our current understanding of both the acidic deposition phenomenon and its associated effects. Previous research focused on long-term or gradual lake and stream acidification and average annual chemistry, rather than on short term (days to months) chemical changes. Now, however, there is growing awareness that superimposed on long-term acidification are episodes during which rapid depressions in pH can occur. Neither the water chemistry changes occurring during episodes nor the long-term effects of acidic deposition on lakes and streams in the United States are well known.

1.2 PROBLEM DEFINITION

The Memorandum of Intent (MOI 1983) on acidic deposition between Canada and the United States included the following summary remarks regarding episodic acidification:

> "While the rate of change of water quality in lakes...is one of the least well-defined aspects of the acidification process, there is evidence that current acid loadings are damaging to fish population and other biota due to short term pH depressions following snowmelt and storm runoff" (MOI 1983, p. 1-3).

Episodic acidification can have significant adverse effects on aquatic biota. For example, Schofield and Trojnar (1980) reported that 50,000 brook trout fry held in a hatchery, which received water from Little Moose Lake in the Adirondacks, perished during a winter thaw when pH levels dropped from about 7.0 to 5.9. Similarly, about 25,000 juvenile rainbow trout held at the Cherokee trout farms in North Carolina were lost following a 5 cm (two inch) rainfall event (Parkhurst et al. 1983). Although these observations confirm that acidification can lead to immediate and severe biological consequences, they also underscore the degree to which fishery resources could be at risk. Even in one small area, economic losses due to effects of acidification on recreational fishing could be significant.

Lakes and streams are hydrologic systems that are driven by hydrometeorological perturbations. Spring snowmelt and storm events represent two major types of acidic loadings to streams and lakes. The significant characteristics of these events include:

- Timing (e.g., season of the year);
- Duration;
- Magnitude (e.g., maximum hydrogen ion concentration);
- Frequency;
- Rate of change in water chemistry variable(s); and
- Overall water chemistry.

1.2.1 Snowmelt Episodes

Snowmelt represents the dominant hydrologic event in many northern systems. Although regional differences exist in both snowmelt patterns and the chemistry of these events, both pH and ANC depressions can be associated with snowmelt. Acidification of lakes and streams during snowmelt has been demonstrated in a number of systems in Europe (Gjessing et al. 1976, Haapala et al. 1975, Henriksen and Wright 1977, Oden and Ahl 1970) and North America (Baird 1984, Galloway et al. 1980, 1983, Jeffries et al. 1979, Jeffries and Snyder 1981, Johannessen et al. 1980, Jones et al. 1984, Schofield 1977). Some of these snowmelt episodes resulted in pH and alkalinity decreases of over one pH unit and 150 ueq/l, respectively, and hydrogen ion increases of over 20 ueq/l.

Acidic pulses during snowmelt can significantly alter the acidic status of lakes and streams. In general, episodic pH and ANC depressions are smaller for systems with lower initial (i.e., pre-melt) pH and ANC values (Marmorek et al. 1986). The greatest chemical changes are expected in waters with moderate ANC, where buffering capacity is low. The acid anions responsible for these pH depressions vary by type (e.g., sulfate or nitrate), as well as spatially and temporally.

Correlations between stream hydrogen ion and snowmelt nitrate or sulfate concentrations vary among systems and among regions. Large nitrate snowmelt pulses, for example, have been correlated with increased stream hydrogen ion concentrations in the Adirondacks (Galloway et al. 1980, Galloway and Dillon 1983, Schofield 1977), New Hampshire (Likens et al. 1976), and the Lac Laflamme watershed in Quebec (Papineau 1984). In the Muskoka-Haliburton streams in Ontario, stream hydrogen ion increases were attributed to increases in both nitrate and sulfate (Jeffries et al. 1979). In the Turkey Lake watersheds, Ontario, there were no significant changes in sulfate and slight changes in nitrate during snowmelt (Jeffries and Semkin 1983). In Scandinavia, most of the nitrate is stored in the watershed and increased stream hydrogen ion concentrations correlate with increased sulfate concentrations (Johannessen et al. 1980, Christophersen et al. 1984). McLean (1981) also concluded that nitric acid was of minimal importance in Ontario and Scandinavia but important in the Adirondacks.

1.2.2 Stormflow Episodes

Rainfall events also can result in acidic pulses to lakes and streams. For example, regular monitoring of Scottish streams has shown that sudden pH and ANC decreases occurred following heavy rain storms (Holden 1979). For many stream and lake systems in regions with minimal or no winter snow pack accumulation, rain storms are the dominant hydrologic events.

It appears that there might be considerable overlap in the geographic areas experiencing both stormflow and springmelt episodes. Acidic episodes associated with storm events have now been recorded for streams in Massachusetts (Eshleman and Hemond 1985), New Jersey (Johnson 1979), Maryland (Bowman 1984), Virginia (Shaffer and Galloway 1982), Pennsylvania (Corbett and Lynch 1982, Hanna 1983), and the Southern Blue Ridge Province (Noggle et al. 1984, Olem 1984, Silsbee and Larson 1981). There is also reason to suggest that the geographic area in which stormflow episodes occur might, in the future, expand. For example, the Southeast streams generally have watersheds that are retaining sulfur inputs (Rochelle et al. 1986) so, in many instances, pH and ANC depressions during storm events might not indicate acidic conditions. There is concern that the sulfate adsorptive capacity of these southeastern watersheds will reach steady-state and sulfate will become a mobile ion and will be transported with cations from the watershed (Johnson, D. W., personal communication).

Constituents other than hydrogen, sulfate, and nitrate ions might also contribute to stormflow episodes. For example, during storm events in Raven Fork, North Carolina, episodes were attributed to organic acids flushed from watershed soils (Noggle et al. 1984). Similarly, Eshleman and Hemond (1985) reported that during summer and fall events, dissolved organic acids played an important role in alkalinity depressions of some small streams draining forested upland watersheds in Massachusetts.

1.3 SITE COMPARISONS

Under the National Acid Precipitation Assessment Program (NAPAP) Task E2, storm event sampling was undertaken during 1984-85 at four locations in the Eastern United States (Figure 1.1):

- Biscuit Brook, New York (Murdoch 1986)
- North and South Fork Bens Creeks, Pennsylvania (Witt and Barker 1986)
- Moses and Jarrett Creeks, North Carolina (Olem 1986)
- East Fork Saline River, Arkansas (Nix et al. 1986)

These four studies collected similar stream and precipitation data, used similar hydrologic and chemical analytical procedures, and had similar QA/QC programs. There is a unique opportunity, therefore, to integrate these studies and investigate similarities and differences in episodic events from streams in the Catskills Mountains, Laurel Hill region, Southern Blue Ridge Providence, and Ouachita Mountains.

The objectives of this study are to:

- Evaluate episodic stream responses at all four sites using uniform procedures;
- Investigate similarities and differences in stream responses at all sites; and

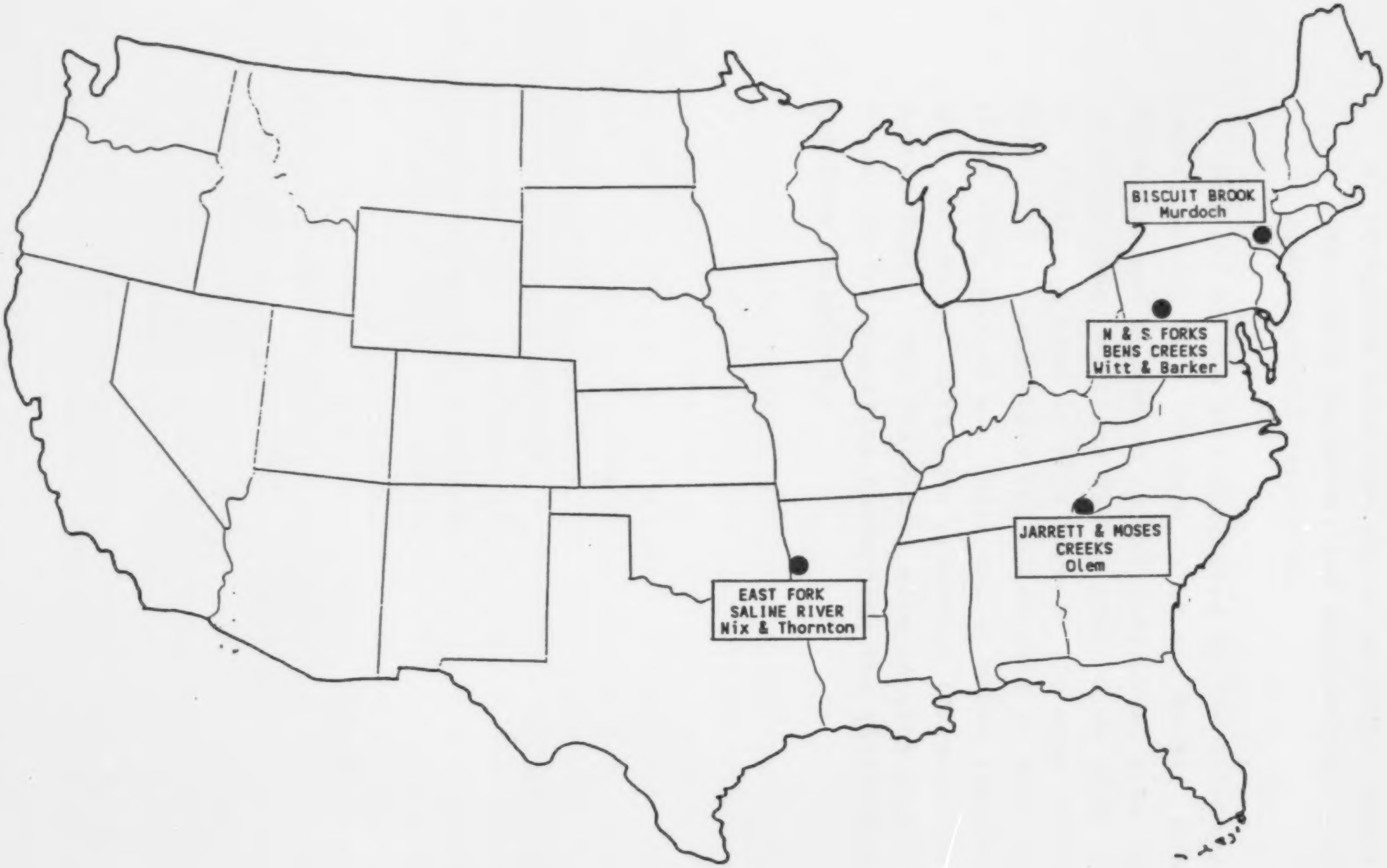
BISCUIT BROOK
Murdoch
N & S. FORKS
BENS CREEKS
Witt & Barker
JARRETT & MOSES
CREEKS
Olem
EAST FORK
SALINE RIVER
Nix & Thornton

Figure 1.1. Location of the four study areas.

- Integrate watershed characteristics, precipitation/deposition patterns, and geochemistry with stream hydrochemical responses.

Not all of the data collected by the Principal Investigators (i.e. Murdoch, Witt and Barker, Olem, Nix and Thornton) and presented in the individual site reports (Murdoch 1986, Witt and Barker 1986, Olem 1986, and Nix et al. 1986) are used in this report. In some instances, the Principal Investigators collected data at more than one site (Olem 1986, Nix et al. 1986) and in other instances more than one year of data were presented (Murdoch 1986, Witt and Barker 1986). The individual site reports should be consulted for specifics concerning the individual systems and data collected.

2.0 STUDY AREAS

Each of the watersheds was selected by the respective Principal Investigators as being representative of the geographic region in which it is located.

Characteristics of each of the study areas are discussed in order from the northern site in the Catskills to the southeastern site in the Ouachita Mountains. For the purpose of this report, Biscuit Brook and North and South Bens Creeks will be considered northeastern streams and Jarrett and Moses Creeks and the East Fork Saline River will be considered southeastern streams.

2.1 PHYSIOGRAPHIC FEATURES

Major physiographic features for each of the watersheds are given in Table 2.1. Although the Ouachita Mountain watershed is somewhat smaller than the other five sites, the watershed areas of all watersheds are roughly equal. The base elevation of the watersheds ranges from about 350 m in the Ouachitas to about 1100 m in the SBRP. The total relief for these watersheds ranges from 300 m in the Ouachitas to about 750 m in the SBRP. The average stream gradients for all the watersheds are steep, ranging from a minimum gradient of about 35 m/km in the Ouachitas to a maximum of 85 m/km in the SBRP. With the exception of the East Fork of the Saline River, however, the stream gradients are similar among streams, averaging about 70 m/km. Stream widths and depths are similar among sites varying between 4 to 6 m wide and less than 0.3 to 0.5 m deep. Biscuit Brook and Moses Creek are the deepest streams. Photographs of the streams are presented in Figure 2-1.

The Biscuit Brook watershed is located approximately 46 km west of the Hudson River and 152 km northwest of New York City in the Catskill Mountains (Figure 1.1). The basin

Table 2.1. Comparison of physiographic characteristics.

	Catskill Mountains	Laurel Hills		SRBP		Ouachita Mountains
	Biscuit Brook	South Fork Bens Creek	North Fork Bens Creek	Jarrett Creek	Moses Creek	East Fork Saline River
State	New York	Pennsylvania		North Carolina		Arkansas
County	Ulster	Somerset		Macon	Jackson	Polk
Drainage Area, km^2	9.9	8.5	8.9	7.8	11.2	6.3
Base Elevation, m NGVD	634	506	408	1156	810	335
Total Relief, m	463	380	427	600	765	300
Stream Gradient, m/km	62	82	63	75	85	34
Stream width[1], m	6	4	5	6	5.5	5
Stream depth[1], m	<0.5	<0.3	<0.3	<0.3	<0.5	<0.3
Stream Order	2nd	2nd	2nd	3rd	3rd	2nd
Forest Cover						
Percent Deciduous	>80	70		90		85
Percent Coniferous	<20	30		10		15

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[1] Estimated during field reconnaissance.

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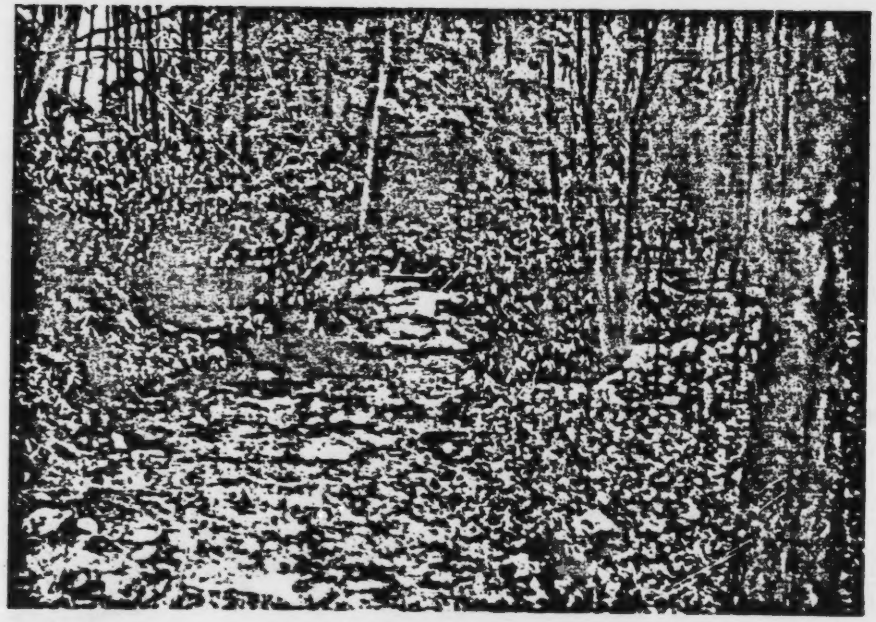
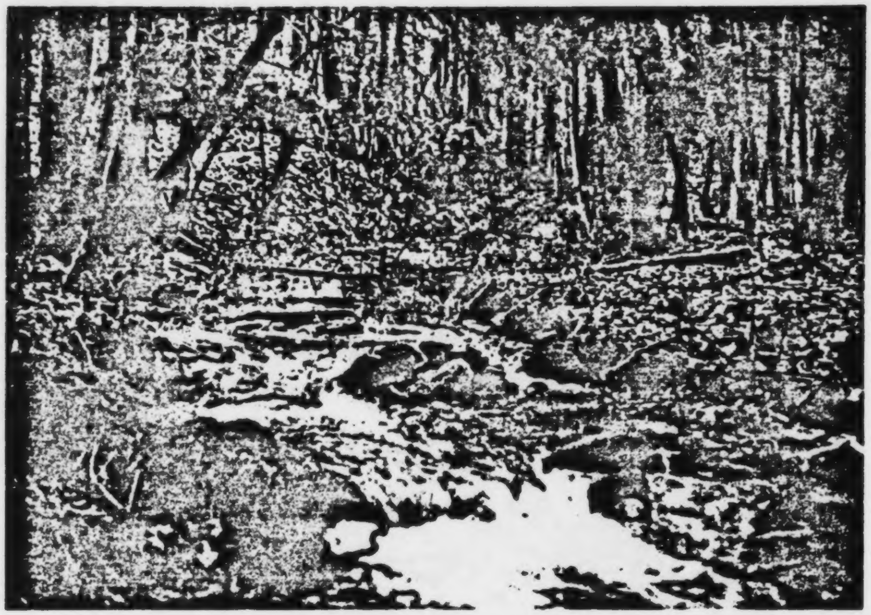
Biscuit Brook, NY

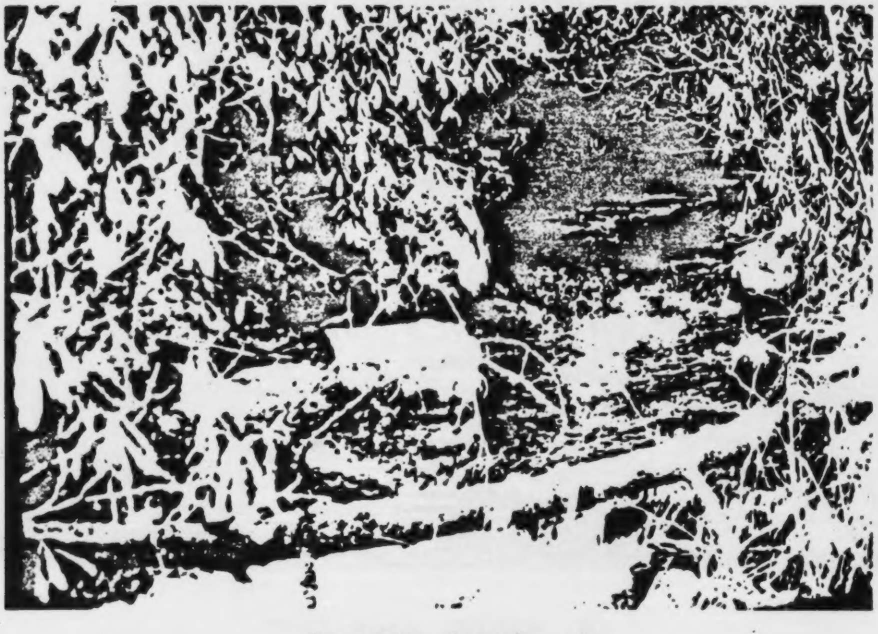


North Fork Bens Creek, PA

Figure 2.1. Photographs of the study sites.

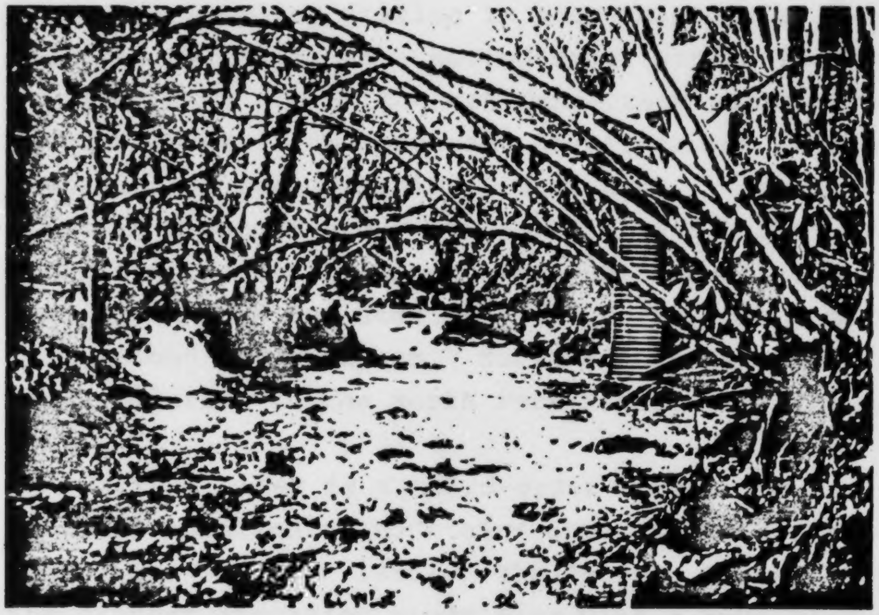


South Fork Bens Creek, PA

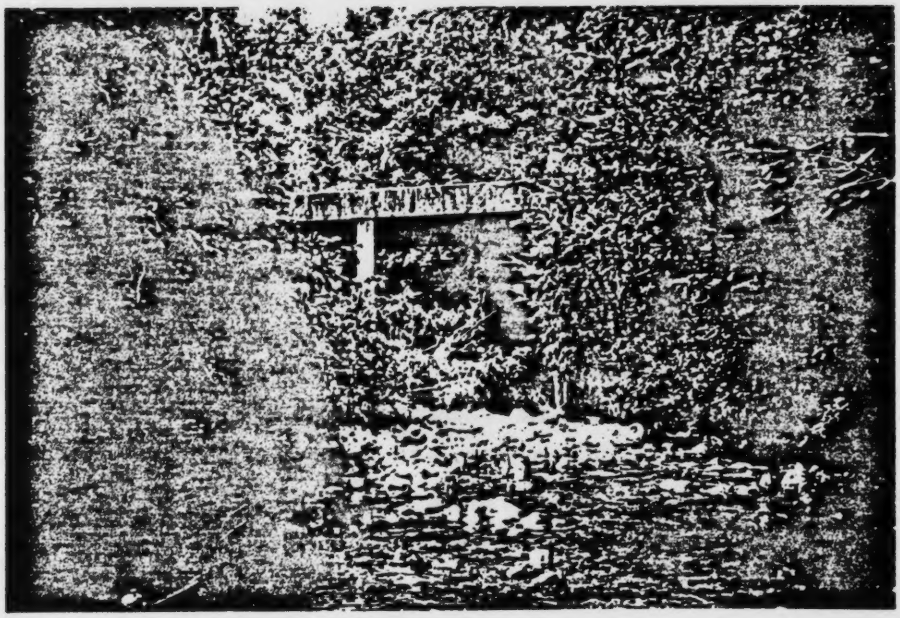


Jarrett Creek, NC

Figure 2.1. Continued.



Moses Creek, NC



East Fork Saline, AR

Figure 2.1. Continued.

above the sampling station is pear-shaped with two small tributaries making it a second-order stream (Murdoch 1986).

The North and South Fork Bens Creek watersheds are located about 82 km southeast of Pittsburgh in the Laurel Mountains of Pennsylvania (Figure 1.1). South Fork Bens Creek is a second-order stream (Witt and Barker 1986). There are two small impoundments upstream of the South Fork Bens Creek sampling station. The North Fork Bens Creek also is a second order stream. North Fork Bens Creek is the primary inflow to the North Fork Reservoir (Witt and Barker 1986).

Jarrett Creek is a third-order stream located in the Southern Appalachian Mountains about 95 km southwest of Asheville, NC (Olem 1986). The Jarrett Creek watershed is the highest elevation study site with a base elevation over 1100 m. Moses Creek also is a third-order stream in the Southern Appalachians about 65 km southeast of Asheville, NC. The base elevation of Moses Creek is above 800 m.

The East Fork Saline River is located in the Ouachita Mountains about 180 km southwest of Little Rock, AR. It is a second-order stream (Nix et al. 1986). The Saline River flows south into Shady Lake immediately below the confluence with the East Fork.

2.2 HYDROMETEOROLOGY

All of the study sites are located in mountainous areas so orographic effects result in variations in precipitation, snowfall, and temperature. The climate varies from humid, continental in the Northeast to sub-humid in the Southeast (Table 2.2). There is a definite temperature gradient from north to south with mean annual air temperatures of 5, 8, 12, and 16°C in the Catskills Mountains (NY), Laurel Hills (PA), Southern Blue Ridge Province (NC), and Ouachita Mountains (AR), respectively (Table 2.2).

Table 2.2. Comparison of climatology.

	Catskill Mountains	Laurel Hill	SBRP	Ouachita Mountains
Climate	Humid Continental	Continental Mountain	Mountainous	Subhumid
Elevation Range, in NGVD	665-1128	506-886	884-1756	335-720
Mean Annual Temperatures, °C	5	8.1	12.4	16.1
Precipitation, cm	157	117	185	133
Mean Annual Snowfall, cm	290	150	30	15
Mean length, freeze free period, days	90-120	150-180	150-180	210

Precipitation ranges from average annual totals of about 120 cm in Pennsylvania to about 185 cm in the SBRP (Table 2.2). Average annual precipitation totals for the Catskill and Ouachita Mountains are about 160 and 130 cm, respectively. There is a gradient in snowfall from about 290 cm in the Catskills to 15 cm in the Ouachita Mountains. The Laurel Hill region receives about 150 cm of snow each year whereas the SBRP sites generally receive about 30 cm.

Precipitation is fairly uniformly distributed throughout the year in the Catskills ranging from a minimum of 10 cm in February to a maximum of 14.6 cm in May (Figure 2.2). Mean annual runoff is about 98 cm or 60 percent of total precipitation. Runoff varies significantly throughout the year from a maximum of about 20 cm in April, (i.e. snowmelt) to a minimum of about 3 cm in August (Figure 2.2).

The mean annual total precipitation in the Laurel Hill area is about 25 percent less than in the Catskills and also is fairly uniformly distributed throughout the year (Figure 2.2). The maximum precipitation of about 13 cm occurs during July with the minimum precipitation of about 8 cm in October. In general, the mean annual runoff is about 51 cm or about 45 percent of the total precipitation. Maximum runoff of about 11 cm occurs during March and corresponds with snowmelt and rainfall. Snowmelt in the Laurel Hill area precedes snowmelt in the Catskills by about a month, which is consistent with the warmer climate. The minimum runoff of about 1 cm occurs during September.

The SBRP receives the greatest amount of precipitation with more rainfall during the winter and early spring months than during late summer (Figure 2.2). The maximum monthly rainfall of about 19 cm occurs during March with a minimum of about 9 cm occurring during October. The average annual runoff is about 78 cm or 48 percent of the total annual precipitation and is fairly uniformly distributed throughout the year (Figure 2.2). The maximum runoff of

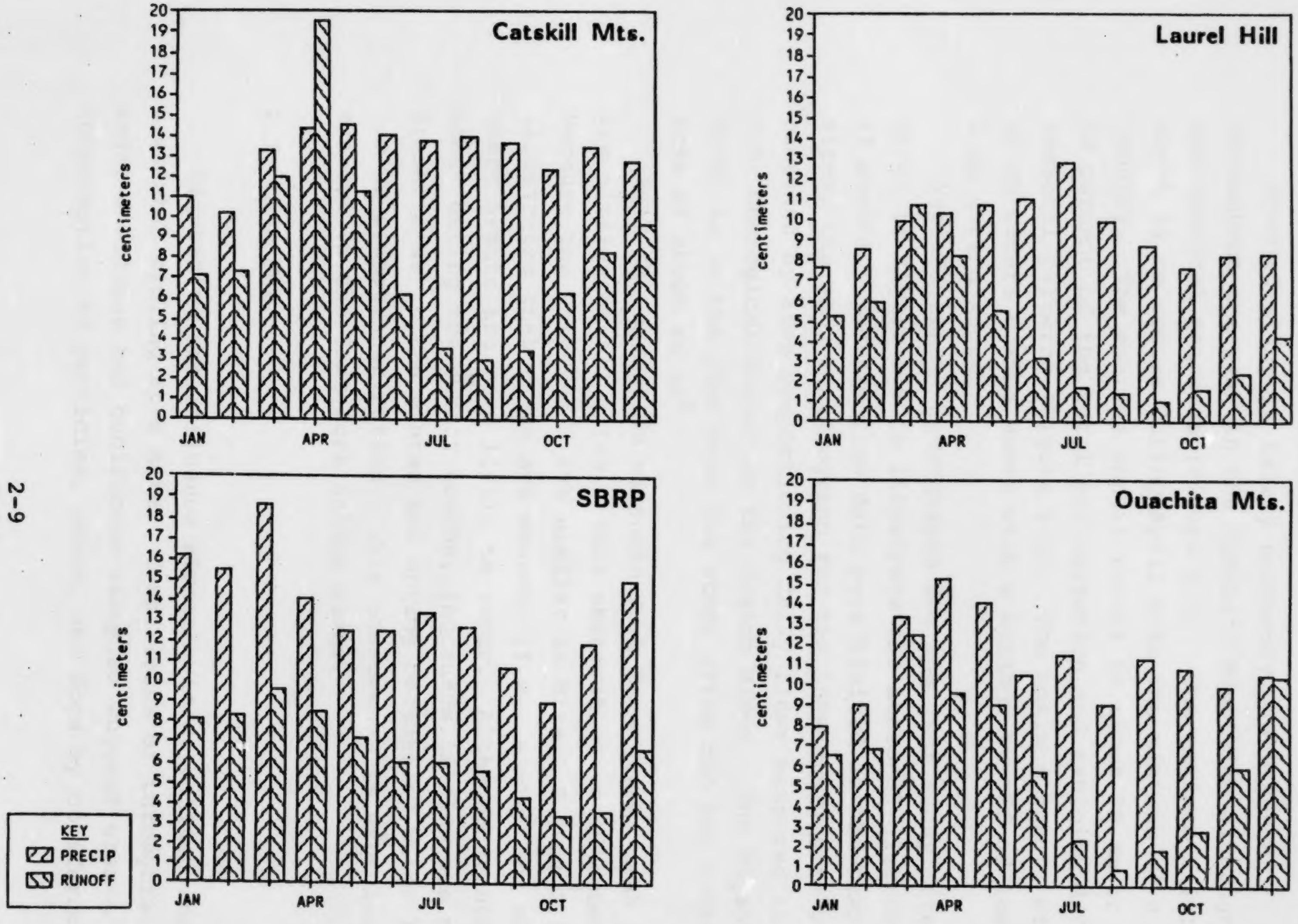


Figure 2.2. Regional average monthly precipitation and runoff for the four study sites.

about 10 cm occurs during March with a minimum runoff of nearly 3 cm during October.

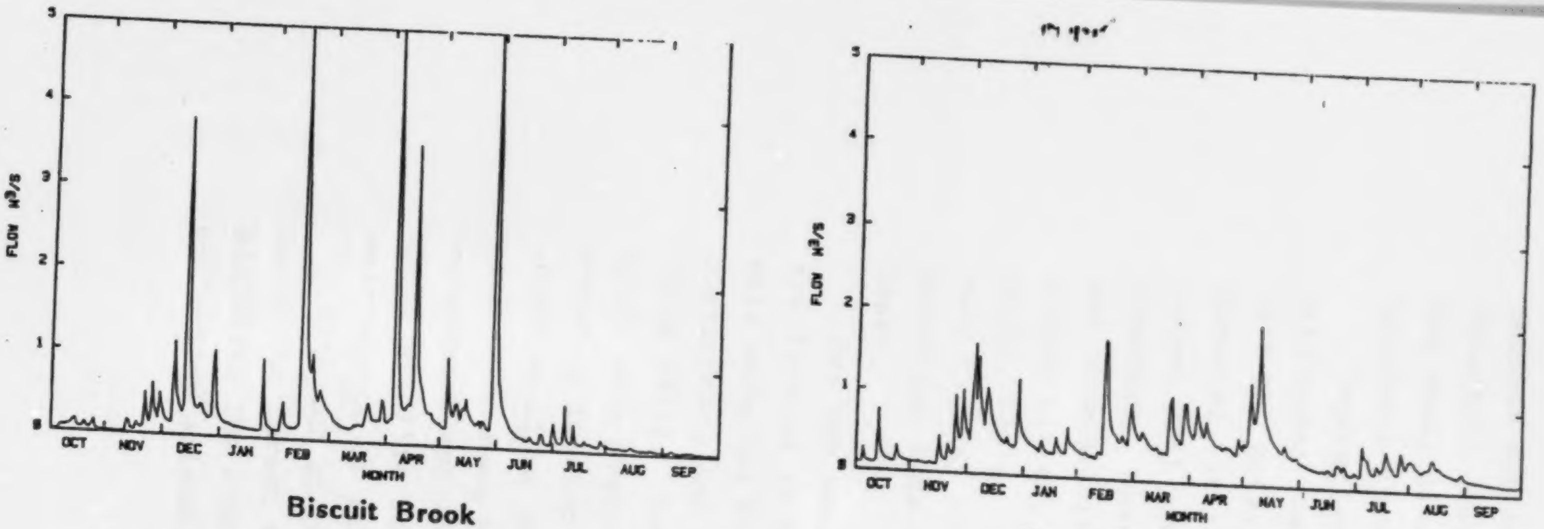
Precipitation is fairly uniformly distributed throughout the year in the Ouachita Mountains although there are seasonal patterns (Figure 2.2). The maximum rainfall of about 15 cm occurs during April with the minimum of 8 cm in January. The average annual runoff is about 75 cm or about 56 percent of the total precipitation and exhibits definite seasonal patterns (Figure 2.2). The maximum runoff of about 12 cm occurs during March with a minimum runoff of less than 1 cm during August.

Typical annual hydrographs for the four study sites are shown in Figure 2.3 to illustrate the seasonal distribution of events. Because flow data were limited at the SBRP study sites, the annual hydrograph for the SBRP study site was computed by area proportioning daily flows measured at a U.S. Geological Survey on the Pigeon River. The Pigeon River is in the SBRP near the study sites and has a drainage area of about 66 km^2.

With the exception of South Fork Bens Creek, peak flows are similar at all sites. This observation is expected because the watersheds are similar in size. Figure 2.3 also illustrates that there are seasons (i.e., winter and spring) where events are more likely to occur. Although events occur during the summer months, increases in flow are not as dramatic as in the winter and spring because of water losses due to evapotranspiration. This phenomenon is especially evident on the East Fork Saline River.

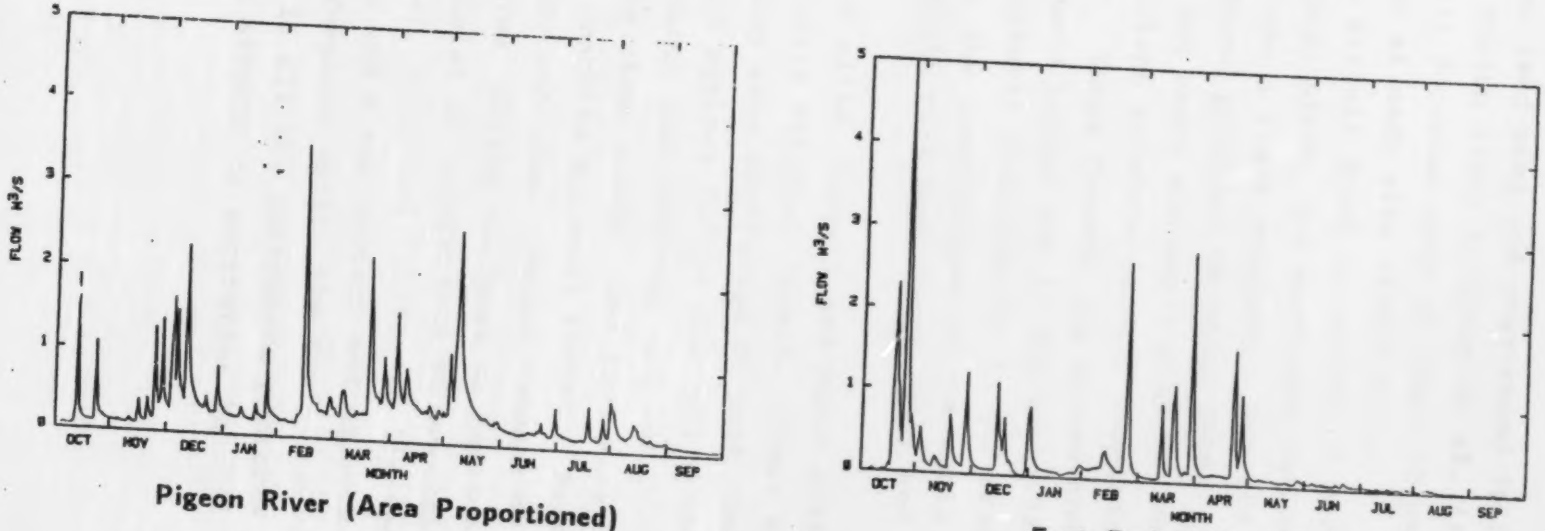
2.3 LAND USE

Vegetation can influence atmospheric deposition and elemental cycling at a site. Comparisons of throughfall under deciduous and coniferous canopies suggest greater interception of particles, gases, and fogs by coniferous



Biscuit Brook

South Fork Bens Creek



Pigeon River (Area Proportioned)

East Fork Saline River

Figure 2.3. Representative annual hydrographs for the four study regions.

forests due to greater leaf area and year-round foliage retention (Mayer and Ulrich 1982, Lindberg et al. 1984). The study sites are all forested with at least 70 percent deciduous forest cover at each site (Table 2.1).

Vegetation in the Biscuit Brook watershed is primarily hardwoods: beech, maple, birch, and scattered hemlock. In 1870 the watershed became a State preserve. Now 100 percent forested, it is considered pristine (Murdoch 1986). The Laurel Hill area also has beech and maple plus oak and chestnut. Where sufficient moisture occurs, mountain laurel and rhododendron occur. These forests are second and third growth timber, having been logged off in the late 1880's and early 1900's. Other cultural disturbances in the area have been minimal except for the construction of two small retention dams on the South Fork Bens Creek (Witt and Barker 1986).

The two southeastern sites, Jarrett and Moses Creeks, are located in the Nantahala National Forest. These sites were selected because they were unaffected by past human disturbance and protected against future disruptive use (Olem 1986). Both deciduous (oak-hickory) and coniferous trees were present in the study areas. The East Fork Saline River is located in the Ouachita National Forest. Forest cover is mixed oak-hickory and pine. Forest management activities have been minimal during the past 40 years and management activities consist of maintenance of several small wildlife food plots. Motorized traffic is limited to maintenance of food plots and a few hunters and campers.

Although species differences exist, the dominance of deciduous forest species in all the watersheds probably minimizes the confounding effects of vegetation in evaluating episodes.

2.4 GEOLOGY

Mineral weathering processes, reactions, and products are important in base cation resupply and neutralization of acidic inputs (Bache 1983, Johnson 1984, Schnoor and Stumm 1984, Church and Turner 1985). Norton (1980) ranked various rock types based on mineral composition and potential weathering rates to identify regional areas potentially susceptible to acidic deposition. Hem (1985) discussed the general relation of lithology (i.e., igneous, sedimentary, and metamorphic rocks) in surface water cation and anion composition. For example, limestone dissolution represents a major source of calcium, whereas feldspar weathering can contribute significant quantities of silica and lesser amounts of calcium, potassium, magnesium, and sodium to surface waters. Precipitation interactions with shales can result in sodium being a dominant cation in surface waters along with chloride or sulfate as a dominant anion (Drever 1982). Metamorphosed sedimentary rocks can produce gneiss and schists, which react with water more like igneous than sedimentary formations (Hem 1985). Site geology, therefore, influences the watershed response to acidic deposition and the resulting surface water chemistry.

The geology of the Biscuit Brook watershed area in New York is composed mainly of uniformly-distributed sandstones, siltstones, and shales. Many of the higher ridges are capped by a resistant layer of arkosic sandstone. Among the detrital rocks such as sandstone, arkoses react similarly to granites (Drever 1982). The sandstone rocks are well fractured and contain minor amounts of silica, calcite, and chematite cement sufficient to greatly increase its resistance to weathering. The feldspars within the sandstone have weathered considerably along exposed surfaces. Feldspar weathering releases potassium, sodium, calcium, and magnesium as primary base cations in addition to silica (Drever 1982).

Above the bedrock and along the mid-slope area in Biscuit Brook lies a thin covering of glacial till. The till deposit is composed of arkosic sandstones, quartz sandstones, quartz pebble conglomerates, siltstones and shales. Whereas most of the till is of local origin, some exotic limestone particles from north of the Catskills might also exist. Apart from weathering and scouring attributed to preglacial and glacial processes, the glacial deposits show relatively little weathering.

In both the South Fork and North Fork Bens Creek, drainage basin geology consists of sandstones of Mississippian Age in the upper parts with the lower part underlain by sandstones of Pennsylvanian age. The rocks are intensely fractured. Within the rock formations, localized layers of limestone and shale also occur. The sandstones are dominantly clean, rounded to well rounded, well sorted, quartz sandstones. The sandstones are poorly cemented by silica and, where outcroppings occur, show signs of being readily weathered. Minor amounts of biotite and mica, together with highly weathered feldspars also are found in the sandstones. Within the inner valley portion of the two watersheds, alluvial deposits of moderately well rounded sandstones, shales, and limestones of cobble size blanket the bedrock.

The geology of Jarrett Creek and Moses Creek watersheds is similar. Jarrett Creek contains biotite schist and gneiss of the Upper Pre-Cambrian Group. Moses Creek contains Muscovite schist and gneiss. Biotite is ferromagnesian (schist that contains iron and magnesium) and Muscovite schist is nonferromagnesian. Biotite schist and gneiss contain sillimanite, graphite, or hornblende and are often found interlayered with micaceous quartz-feldspar (metasandstone). Biotite schist and gneiss are less often interlayered with amphibolite, hornblende, and schist fragments. Moscovite schist and gneiss contain mica-quartz-plagioclase schist that is usually interlayered with genissic micaceous metasandstone. The schist is graphitic and/or sulfidic bearing (Olem 1986).

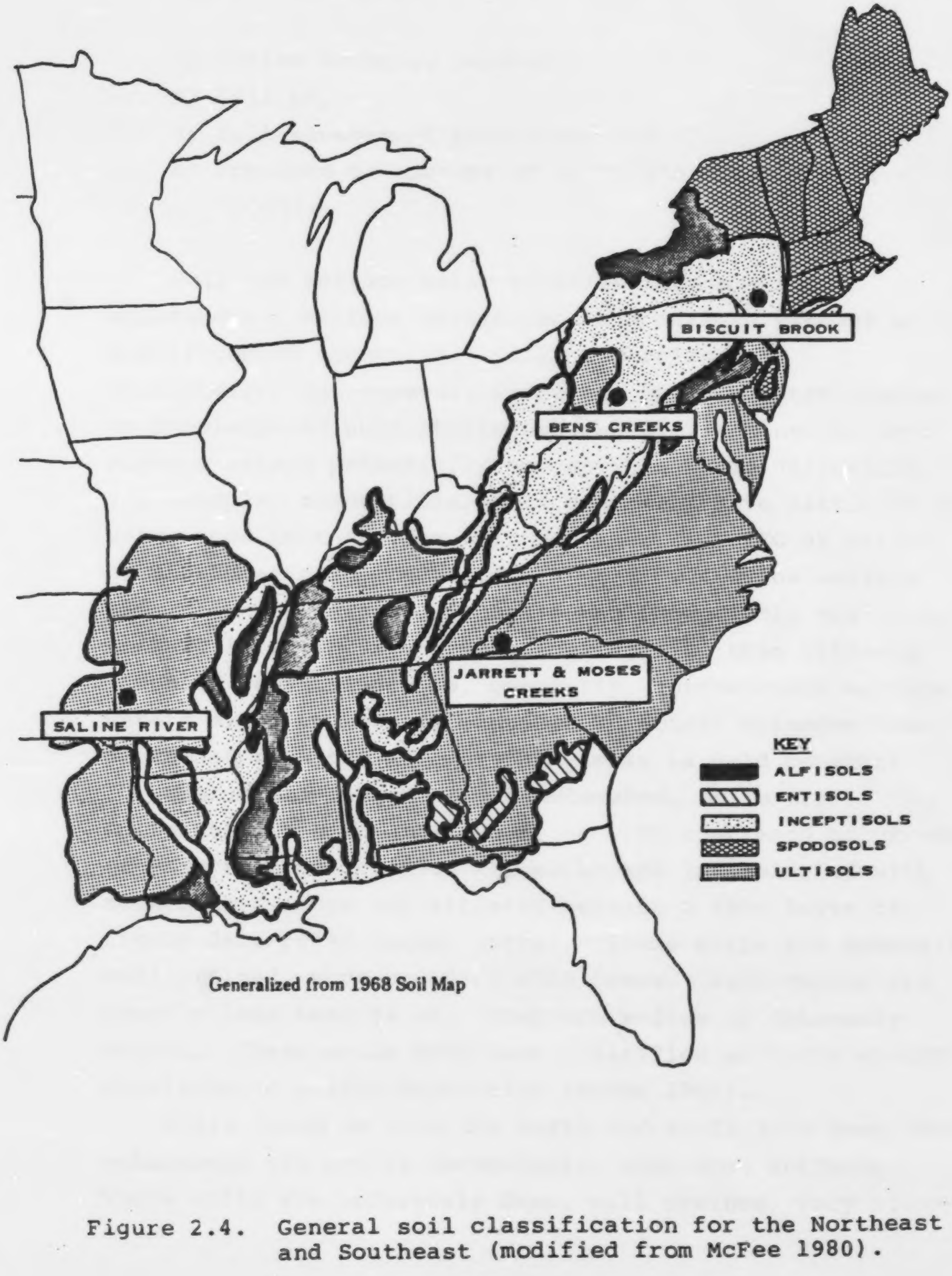
The Ouachita Mountain study area shows the extensive folding and faulting of deposited sediments, which occurred during the upper Paleozoic. Minor metamorphism related to the uplift also has had an effect on the mineralogic constituents. The dominant geologic formations in both watersheds are Arkansas Novaculite and Stanley Shale.

The Arkansas Novaculite of Devonian and early Mississippian age is extremely resistant and is the major ridge-forming formation within the study area. Approximately 65% of the surface geology within the East Fork Saline River watershed are composed of Arkansas Novaculite. The formation also contains minor amounts of chert, shale, and sandstone.

Stanley Shale is the dominant valley forming material in the study area. It represents approximately 25% of the surficial geological material found in the East Fork Saline River watershed (Nix et al. 1986). The Stanley Shale of Mississippian age is composed mostly of shale with lesser quantities of thin to massive, fine-grained, feldspathic sandstone (Stone and Bush 1984).

2.5 SOILS

The two northeastern watersheds contain soils that are predominantly Inceptisols whereas the two southeastern watersheds contain primarily Ultisols (Figure 2.4). Regions dominated by Ultisols, Spodosols, and some of the Inceptisols encompass most of the areas predicted to be susceptible to acidic deposition (McFee et al. 1984). McFee


BISCUIT BROOK
BENS CREEKS
JARRETT & MOSES CREEKS
SALINE RIVER
KEY
ALFISOLS
ENTISOLS
INCEPTISOLS
SPODOSOLS
ULTISOLS

Generalized from 1968 Soil Map

Figure 2.4. General soil classification for the Northeast and Southeast (modified from McFee 1980).

(1980) classified soil sensitivity to acidification based on four soil properties:

1) Cation exchange capacity,
2) Soil pH,
3) Soil management practices, and
4) Presence or absence of carbonates in the soil profile.

Soil and surface water acidification are not synonomous. Surface waters can be acidified without soil acidification occurring. Soil properties and characteristics, however, influence surface water chemistry so knowledge of soil attributes can provide insight into surface waters potentially susceptible to acidification. For example, susceptible soils generally have little or no carbonates in the upper soil horizons, low CEC or percent base saturation but a pH of 5.5 to 6.0, and low sulfate adsorption capacity. Spodosols and Inceptisols are thought to have lower sulfate adsorption capacity than Ultisols (Johnson et al. 1980) so, generally, northeastern surface waters might be more susceptible to acidic episodes than southeastern sites if everything else is held constant.

Within the Biscuit Brook watershed, soils are dominantly thin Inceptisols along with scattered occurrences of very thin Spodosols. All soils are intermingled with rock outcroppings and situated beneath a thin layer of highly decomposed forest litter. These soils are generally well drained, very bouldery silt loams. Soil depths are usually less than 50 cm. They are medium to extremely acidic. These soils have been classified as being slightly sensitive to acidic deposition (McFee 1980).

Soils found in both the North and South Fork Bens Creek watersheds are mostly Inceptisols, with some Entisols. These soils are moderately deep, well drained, very stoney silt loam to silt loam. They are formed predominantly in residual sandstones and shales, and within colluvial material along the lower slopes and alluvium within the inner valley region. Depths commonly extend to near 100 cm beneath a thin layer of forest litter. The soils are acidic, with pH values of 3.6 to 5.5. Soils common to this region have been classified as being slightly sensitive to acidic deposition (McFee 1980).

Inceptisols and Ultisols comprise the majority of soils found within the Jarrett and Moses Creek watersheds. These soils were formed in residual material composed of biotite and muscovite schist, and gneiss. The biotite schist is found mainly in the Jarrett Creek areas while muscovite schist is found in the vicinity of Moses Creek. Soils of this area are classified as stoney sandy loams with increased clay accumulations in certain localities, well drained, ranging from 50 to 110 cm in depth. They are acidic soils with pH values of 4.0 to 5.5. Soils common to this area have been classified as being slightly sensitive to acidic deposition (McFee 1980).

The soils found within the Saline River study area are characteristic of soils formed in forested regions under humid climatic conditions. The soils are predominantly highly weathered Ultisols, generally acidic with pH values of 4.0 - 5.5. The soils have low to moderate base saturation and low cation exchange capacity. The soils are classified as silty loam in the upper horizons to gravelly loam near the base. All of the soils possess a lithic or paralithic contact of fractured shale, sandstone, or chert. Thicknesses are generally less than a meter. These soils are typically well drained, with rapid runoff and moderate to moderately rapid permeability. These soils were not included in the classification of McFee (1980) but would probably be classified as slightly sensitive.

2.6 REGIONAL QUALITY PATTERNS OF PRECIPITATION

Regional patterns in the pH of wet deposition and in sulfate concentrations are shown in Figures 2.5 and 2.6, respectively. The Laurel Hill watersheds are located in a region with high precipitation sulfate concentrations and low pH. The Catskills and SBRP both lie in a region with intermediate wet deposition sulfate concentrations and pH while the Ouachita Mountains are located in a region with the lowest wet deposition sulfate concentrations and highest pH values of any of the regions. All regions, however, had rainfall pH values less than 5.0. Sulfate deposition appears to be increasing in the Southeast (NAS 1986).

All of the watersheds studied in this project are located in areas that have low alkalinity surface waters (Figure 2.7). These areas correspond with surface regions that were sampled or are being sampled in the National Surface Water Survey (NSWS Phase I).

2.7 FISH RESOURCES

All four sites have fish. Biscuit Brook contains populations of brook trout (Salvelinus fontinalis), brown trout (Salmo trutta) and sculpin (Cottus sp.). This stream drains south into the West Branch Neversink River and subsequently southwest into the Neversink Reservoir and the Delaware River. The Neversink River is famous for its sport fishery (Murdoch 1986) and has recently developed a landlocked salmon fishery through a restocking program (P. Murdoch, personal communication).

In both the North and South Forks Bens Creek, native brook trout (S. fontinalis) and mottled sculpin (C. buirdi) were observed (J. Barker, personal communication). South Fork Bens Creek also is stocked with brook trout.

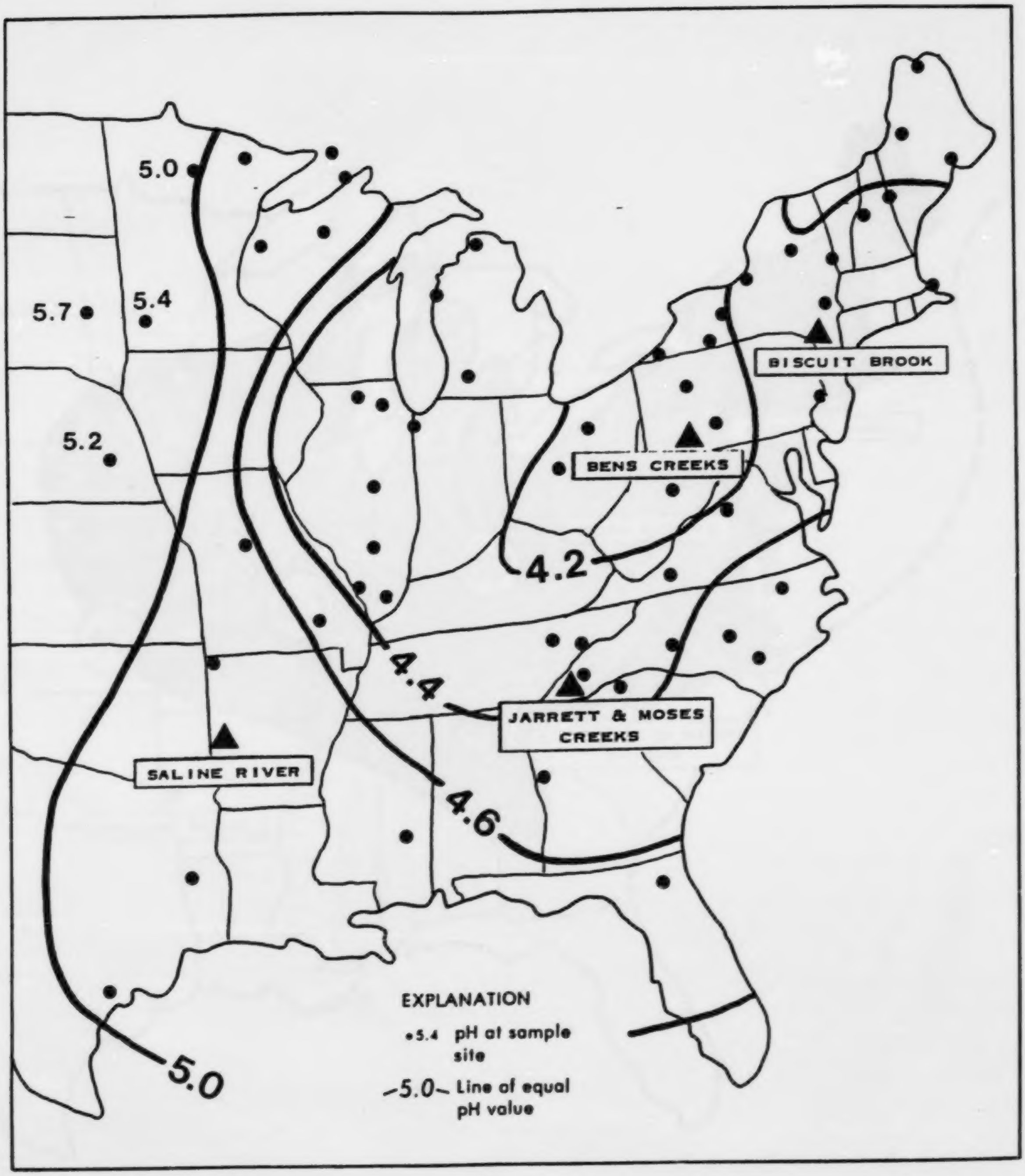

5.0
5.7
5.4
5.2
BISCUIT BROOK
BENS CREEKS
4.2
4.4
JARRETT & MOSES CREEKS
SALINE RIVER
4.6
5.0
EXPLANATION
•5.4 pH at sample site
-5.0- Line of equal pH value

Figure 2.5. Wet deposition pH isopleths for 1980-82 (modified from 1983 Annual NAPAP Report).

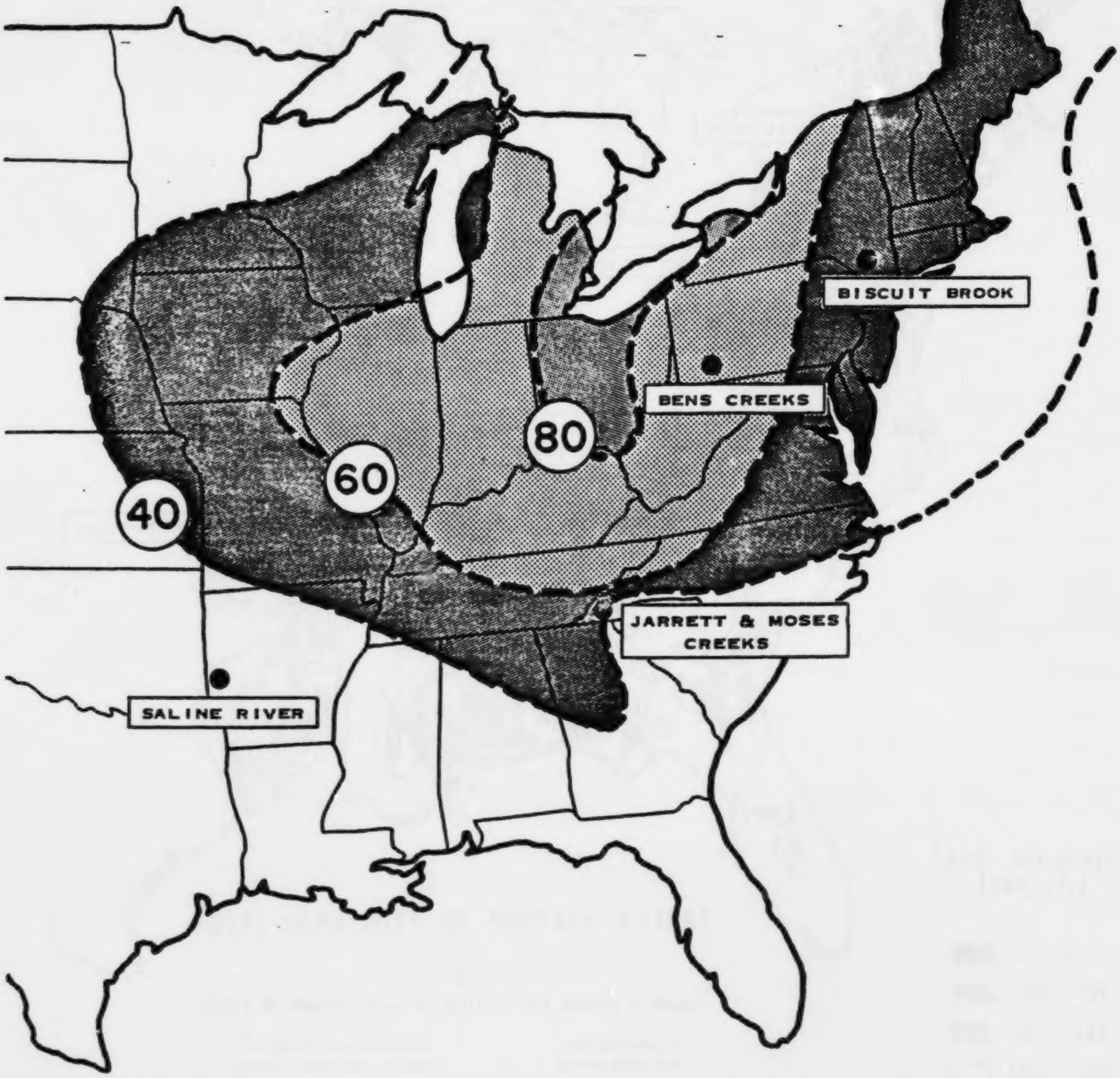
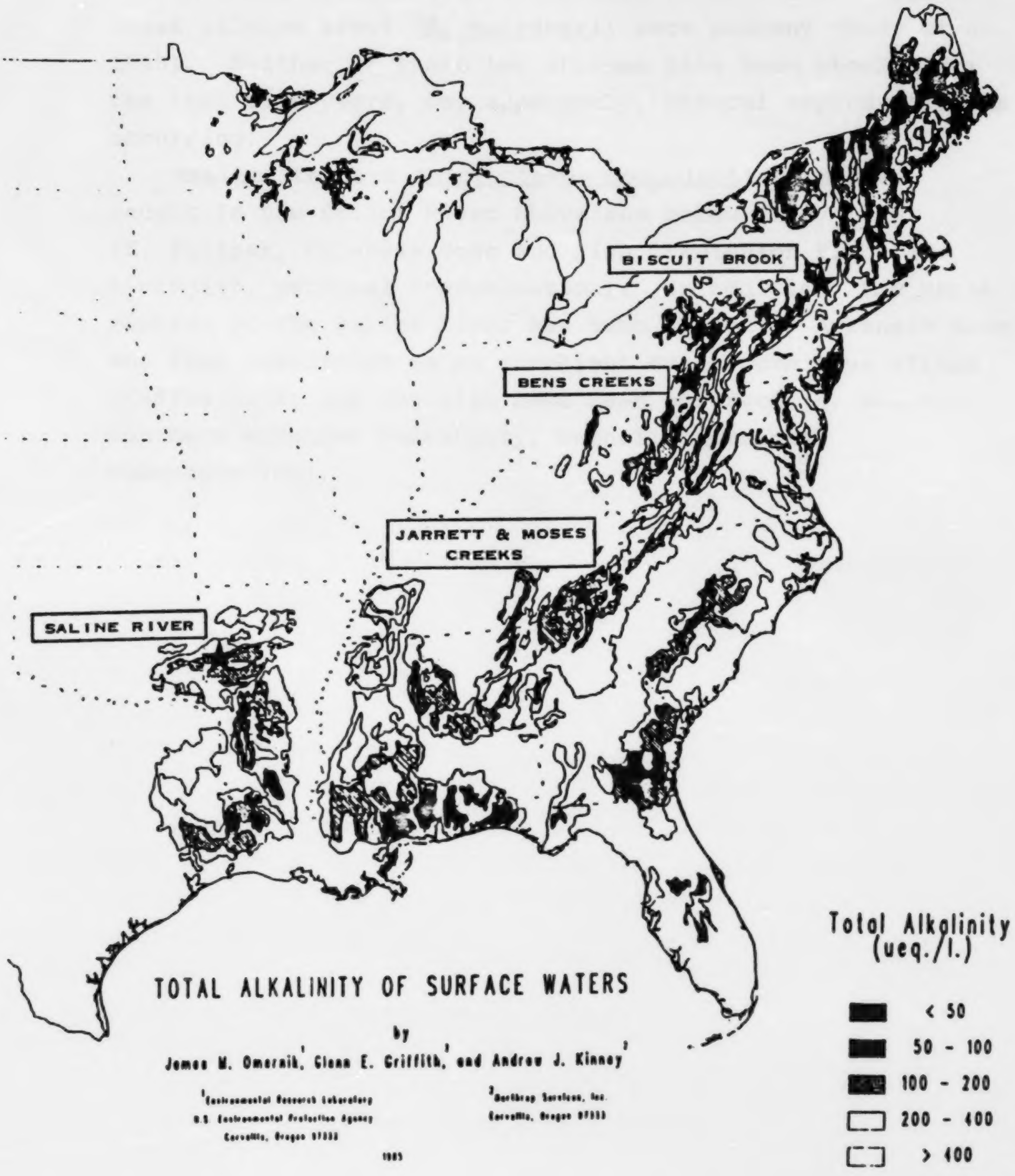

BISCUIT BROOK
BENS CREEKS
80
60
40
JARRETT & MOSES CREEKS
SALINE RIVER

Figure 2.6. 1980 weighted average sulfate ion concentrations (ueq/l) for wet deposition samples (adapted from Barrie et al. 1982).



BISCUIT BROOK
BENS CREEKS
JARRETT & MOSES CREEKS
SALINE RIVER
TOTAL ALKALINITY OF SURFACE WATERS
by
James M. Omernik[1], Glenn E. Griffith[1], and Andrew J. Kinney[2]
[1]Environmental Research Laboratory
U.S. Environmental Protection Agency
Corvallis, Oregon 97333
[2]Northrop Services, Inc.
Corvallis, Oregon 97333
1985
Total Alkalinity (ueq./l.)
< 50
50 - 100
100 - 200
200 - 400
> 400

Figure 2.7. Total alkalinity map of the Eastern United States (after Omnerik et al. 1986).

In Moses Creek, brook trout were present and in Jarrett Creek rainbow trout (*S. gairdneri*) were present (Hudy et al. 1985). Neither of these two streams have been stocked for the last five years, so, apparently, natural reproduction is occurring.

Smallmouth bass (*Micropterus dolomieui*) have been caught in the Saline River above and below Shady Lake (S. Filipek, Arkansas Game and Fish Commission Fisheries Biologist, personal communication). In addition, the upper portion of the Saline river has been listed by Arkansas Game and Fish Commission as an excellent smallmouth bass stream (Kaffha 1979) and the fish have been observed (H. Robison, Southern Arkansas University, Magnolia, personal communication).

3.0 METHODOLOGY

Comparable methods were used at each site to measure and analyze both quantity and quality of precipitation and streamwater. This section will discuss these methods, the sampling frequency, and any major differences among sites. Numerous water quality variables were analyzed in each of the samples. This report will focus primarily on pH, ANC, base cations (Ca, Mg, Na, K), acid anions (SO_4, NO_3, Cl) and dissolved aluminum.

3.1 WET DEPOSITION

Rainfall quantity was measured by means of continuous recording rain gages located at each study site over the interval shown in Table 3.1. Samples for wet deposition quality were collected at the Biscuit Brook, South Fork Bens Creek, and the East Fork Saline study sites using NADP/NTN protocols. Biscuit Brook is part of the NADP/NTN monitoring network. Precipitation quality data for Jarrett and Moses Creeks were obtained from the NADP/NTN monitoring station at Coweeta, NC, which is located within 65 km of both sites. For consistency with NADP/NTN results, NADP protocol was used to define seasons throughout this report. The appropriateness of this convention is discussed in Section 5.2. This convention is:

- Winter = December, January, February
- Spring = March, April, May
- Summer = June, July, August
- Fall = September, October, November

Table 3.1. Precipitation quantity and quality sampling intervals.

SITE	Quantity		Quality	
	Recording Interval	Location of Rain Gage(s)	Recording Interval	Location of Wet Collector(s)
1. Biscuit Brook	Continuous Water Years 1983-1985	on-site	Weekly (NADP)	on-site
2. South Fork Bens Creek	Continuous Water Years 1984-1985	on-site	WY 84: Weekly WY 85: Intermittent	on-site
3. Jarrett/ Moses Cr.	Continuous (Supplemented for missing data)[1]	on-site	Weekly (NADP)	Coweeta Sta.
4. East Fork Saline R.	Continuous Nov 84-Oct 85	on-site	Weekly Samples Nov 84-Oct 85	on-site

---

[1] Missing data obtained from adjacent stations and relationships between stage and precipitation.

3.2 FLOW MEASUREMENTS

Stream stage was recorded continuously at each study site. Stage-discharge relationships were developed by the individual investigators to compute flows for Biscuit Brook, North and South Fork Bens Creek, and the East Fork Saline River. These flows were used for this study.

Daily flows for Jarrett and Moses Creek were not previously computed because of limited discharge measurements. In order to use the available stage records, stage-discharge relationships were developed using: 1) Snyder unit hydrograph procedure (Viessman et al. 1972); 2) data from similar but downstream gaged streams in the area of Jarrett/Moses Creeks; and 3) SCS hydrograph techniques (DABRO - Golding, 1982). The daily discharge estimates for Jarrett and Moses Creeks were compared with daily and monthly runoff values from two USGS sites in the vicinity of Jarrett and Moses Creeks. A detailed description of the discharge calculations for Jarrett and Moses Creeks is included as Appendix A.

3.3 STREAM CHEMISTRY

Stream chemistry sample type, frequency, and collection method for each of the study sites are described in Table 3.2. Automatic, stage-activated stream samplers were used to collect event data in the Jarrett, Moses, and Bens Creeks studies. Auto-samplers also were used to collect some of the event data in the Biscuit Brook study, but were activated by local cooperators. Most of the Biscuit Brook stream chemistry samples were hand-collected. All storm event stream samples for the Saline study were collected by hand. Grab sampling was used to collect baseflow samples at all four sites.

Table 3.2. Sampling procedures for stream chemistry at each site.

Study	Sample Type	Sampling Frequency	Interval (dates)	Collection Method(s)
Biscuit Brook	Base Flow	At Least Monthly	Apr 83-Nov 85	Grab
	Storms	Selected		Grab/Auto-Sampler
North Fork Bens Creek	Base Flow	Monthly	Oct 83-Mar 86	Grab
	Storms	Selected		Auto-Sampler
South Fork Bens Creek	Base Flow	Monthly	Oct 83-Oct 85	Grab
	Storms	Selected		Auto-Sampler
Jarrett Creek	Base Flow			
	pH	At Least Monthly	May 84-Aug 85 and Apr 85-May 85	In Situ
	Other Variables	Quarterly	Dec 83-Nov 84 and May 85	Grab
	Storms	Selected		Auto-Sampler
Moses Creek	Base Flow			
	pH	At Least Monthly	May 84-May 85	In Situ
	Other Variables	Quarterly	Dec 83-May 85	Grab
	Storms	Selected		Auto Sampler
E. Fork Saline	Base Flow	Bi-Weekly	Jul 84-Nov 85	Grab
	Storms	Selected		Grab

The sample treatment and preservation techniques used in each study followed protocols documented as part of the National Surface Water Survey - Phase I (Drouse' et al. 1985).

3.4 LABORATORY ANALYSIS AND QUALITY CONTROL

The water quality variables measured in each sample are listed in Table 3.3. Analytical procedures used in each study followed the NSWS-Phase I protocol (Hillman et al. 1986). These procedures were designed to insure the integrity of each low-ionic strength precipitation and stream sample.

Similar EPA-approved internal and external quality control/quality assurance programs were maintained during each study by each analytical laboratory and each study group. One important exception to this exists regarding the analyses for North and South Bens Creeks. These analyses were performed according to USGS standard methods (Skougstad et al. 1979). Thus, for example, alkalinity was reported only down to 10 ueq/l (i.e., 0.5 mg/l as $CaCO_3$) with, apparently, a precision of 0.5 mg/l as $CaCO_3$. Use of this procedure complicated efforts of interpretation of alkalinity changes during events.

Stream chemistry analyses for the Biscuit Brook and Bens Creeks studies were performed in USGS Laboratories. Precipitation analyses for the Bens Creek study also were performed in USGS Laboratories. Precipitation analyses for the Biscuit Brook study were performed at the NADP/NTN Laboratory in Illinois. The TVA Water Quality Laboratory, Chattanooga, TN provided analytical support for the Jarrett and Moses Creek studies. Sample analyses for the Saline project were performed in the Ouachita Baptist University, Water Quality Laboratory, Arkadelphia, AR.

Table 3.3. Water quality variables measured at each site.

Location	Biscuit Brook	Bens Creeks	Jarrett/ Moses	E. Fork Saline
Water Temperature	x		x	x
Field pH	x(P)[1]	x(P)	x	x
Dissolved oxygen			x	x
Spec. Conduct. (Field)		x	x	x(P)
Spec. Conduct. (Lab)	x(P)[1]	(P)	x	
Turbidity				x
Lab pH*	x(P)[1]	(P)	x(P)[2]	x(P)
Strong Acidity		x(P)	x	x
Weak Acidity		x(P)	x	x(P)
Apparent Color			x	
True Color			x	x
Hardness		x		
Gran Alkalinity*	x	x	x	x(P)
Bromide	x	x(P)		
Chloride*	x(P)[1]	x(P)	x(P)[2]	x(P)
Fluoride	x	x(P)	x	
Sulfate*	x(P)[1]	x(P)	x(P)[2]	x(P)
Nitrate Nitrogen*	x(P)[1]	x	x(P)[2]	x(P)
Dissolved Organic Carbon	x	x	x	x(P)
Monomeric Aluminum				x
Dissolved Aluminum*	x	x(P)	x	x(P)

Table 3.3. Continued.

Location	Biscuit Brook	Bens Creeks	Jarrett/ Moses	E. Fork Saline
Organically Complexed Aluminum				x
Ammonia Nitrogen	x(P)[1]	x	x(P)[2]	x(P)
Total Kjeldahl Nitrogen				x
Total Phosphorus				x(P)
Total Dissolved Phosphorus	x(P)[1]	x	x	x(P)
Ortho Phosphate		x(P)		
Silica	x	x(P)		x
Sodium*	x(P)[1]	x(P)	x(P)[2]	x(P)
Magnesium*	x(P)[1]	x(P)	x(P)[2]	x(P)
Calcium*	x(P)[1]	x(P)	x(P)[2]	x(P)
Potassium*	x(P)[1]	x(P)	x(P)[2]	x(P)
Iron	x	x(P)		
Manganese	x	x(P)		

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x Stream samples

P Precipitation

[1] NADP Data - Biscuit Brook Station, NY

[2] NADP Data - Coweeta Station, NC

* Variables specifically discussed in this document

3.5 MASS BUDGETS

Annual inputs (wet deposition only) and outputs for hydrogen, sulfate, nitrate, sum of major anions plus ANC, and the sum of base cations were calculated for each watershed. Because one of the objectives of these computations was to make comparisons among sites, a consistent methodology had to be used for all budget calculations.

Data limitations at some of the sites dictated that the computations be based on seasonal volume weighted precipitation chemistry and flow weighted stream chemistry. Annual budgets were obtained by multiplying the weighted chemistry for a specific season by the total volume of precipitation and flow occurring during that same season. The total masses for each season then were summed for an annual estimate.

The availability of multiple years of data at Biscuit Brook and South Fork Bens Creek allowed selection of a year of data that was similar to the other sites with respect to hydrometeorological conditions. The time intervals over which mass budgets were determined for each study watershed are:

- Biscuit Brook: October 1983-September 1984
- South Fork Bens Creek: October 1983-September 1984
- Jarrett Creek: May 1984-March 1985
- Moses Creek: May 1984-March 1985
- Saline: November 1984-October 1985

In general, these time intervals tended to be wet compared to normal conditions (Section 4.1).

Data availability resulted in two deviations concerning the budget computations. First, because only eleven months of data were available on Moses and Jarrett Creeks, these budgets were multiplied by a factor of 1.1 (12 months/11 months) to compensate for the missing month of data. Second, spring and summer nitrate (and associated flow) data for South Fork Bens Creek were limited for the year selected to be analyzed in this report so all available nitrate data were used to determine flow-weighted seasonal concentrations. Third, when data were reported as less than a specific value or detection limit, one-half of that value was used.

4.0 RESULTS

This section discusses and compares water budgets, wet deposition chemistry, baseflow stream chemistry, episodes, and mass budgets for each study site.

4.1 WATER BUDGETS

During water year 1984 (WY84 is Oct 83 - Sep 84), the Biscuit Brook watershed received 168 cm of precipitation. This was slightly greater than the 32 year average of 157.2 cm at Slide Mountain, which is adjacent to the study site. In general, April and May were abnormally wet. June through September were dry. Runoff for the water year averaged 110.8 cm or 66 percent of precipitation. Maximum monthly runoff (25.7 cm) occurred in April and exceeded April precipitation (21.1 cm) indicating the possibility of snowmelt. Runoff in February (20.2 cm) also exceeded precipitation (17.8 cm). The peak instantaneous discharge for WY84 was 22.7 m^3/s on April 5, 1984 and the minimum was less than 0.03 m^3/s in both October 1983 and September 1984.

WY84 at the South Fork Bens Creek was wet with 148.8 cm of precipitation compared to the long-term average of 116.8 cm. Although all seasons, except fall, were abnormally wet, there was significant monthly variability with a wet month followed by a dry month and then a wet month again. Runoff for the water year averaged 92.2 cm or 62 percent of precipitation. The peak discharge of the water year was 3.2 m^3/s in February during snowmelt. Minimum flows of less than 0.03 m^3/s occurred in September, October, and November.

Although precipitation and flow data were limited at the SBRP sites, historical precipitation data from surrounding NOAA weather stations indicated the study period was wet during all seasons except fall, when precipitation values were near normal. Precipitation in this region was highly variable and specific sites might not follow this general pattern. Comparison of generated flows with precipitation totals resulted in runoff to precipitation ratios of 0.87 and 0.78 for Jarrett and Moses Creek, respectively. Although these values appeared high, comparisons with nearby U.S. Geological Stations gaging stations, indicated they were realistic (Appendix A). Local variability in precipitation also might account for some variability. Runoff ratios varied from 0.3 during the fall to 1.0 and above during the winter and spring.

During the study year for the East Fork Saline River (Nov 84 - Oct 85), precipitation was near normal to slightly above normal. The site-specific total of 152 cm of precipitation was slightly higher than the basin average for the study year of 131.5 cm and the basin norm of 133.1 cm, again indicating the spatial variability found in mountainous areas. All seasons were near normal except the summer, which tended to be dry. Runoff averaged 53 percent of precipitation for the year varying from a maximum near 76 percent during the spring to a minimum of 26 percent during late summer and early fall. The peak discharge on the East Fork was in early April with the minimum less than 0.03 m^3/s from August through October.

4.2 WET DEPOSITION CHEMISTRY

Factors influencing the effects of acidic deposition on surface water chemistry are the deposition chemical composition, and spatial and temporal variability. The regional concentrations were obtained by volume-weighting data from NADP/NTN monitoring stations within a 400 km radius of each of the study sites. The stations used are listed in Appendix B. Because wet deposition chemistry were not available at Jarrett and Moses Creek sites, data from the NADP/NTN station at Coweeta were used for these sites. These data will be referred to as Coweeta data. Components of wet deposition are discussed in this section and summarized in Tables 4.1 and 4.2 and Figures 4.1 and 4.2.

4.2.1 Composition

The pH, base cations, and major acid anions have been summarized for each site by season and are listed with the corresponding NADP/NTN regional concentrations in Table 4.1. The annual and seasonal average concentrations for each site generally were similar to the corresponding regional values or within the range of values. Seasonal and annual wet deposition pH values typically were lower in the Saline and South Fork Bens Creek watersheds than the corresponding regional values. These two sites generally had higher concentrations of each of the base cations and acid anions than concomitant regional constituent concentrations.

The seasonal and annual pH values at the Biscuit Brook and SBRP sites were slightly higher than the comparable regional values. Seasonal and annual base cation concentrations at these two sites were similar to the corresponding regional concentrations but the sulfate and nitrate concentrations at each of these sites were typically less than the regional averages, which correlates with slightly higher deposition pH values.

Calcium and sodium were the dominant base cations at all sites (Figure 4.1). The order of increasing average annual base cation concentrations in all regions was K < Mg < Na < Ca, except for the East Fork Saline River site, where sodium concentrations were greater than calcium. At the South Fork Bens Creek site, sodium concentrations were almost twice the concentration at the Biscuit Brook site, although on a regional basis they were about equal (Table 4.1). Wet deposition at the East Fork Saline River site was observed to have 1.5 to 3.0 times as much sodium as the other sites and at the regional level the Ouachita region was observed

Table 4.1. Comparison of site and regional wet deposition comparisons.

BISCUIT BROOK, NY

	Winter		Spring		Summer		Fall		Annual	
	Dec 83 - Feb 84		Mar 84 - May 84		Jun 84 - Aug 84		Sep 84 - Nov 84		Jan 84 - Dec 84	
	Site	Region	Site	Region	Site	Region	Site	Region	Site	Region
Precipitation, cm	39.29	29.55	53.80	40.10	29.52	35.57	21.06	19.15	133.12	117.11
pH, s.u.	4.73	4.55	4.62	4.39	4.24	4.20	4.36	4.36	4.36	4.31
Base Cations										
Ca, ueq/l	2.00	4.99	6.99	7.49	2.99	4.99	6.99	6.49	5.99	6.48
Mg, ueq/l	1.73	4.11	2.47	3.29	1.56	2.47	4.61	4.11	3.04	3.29
K, ueq/l	0.28	0.51	1.66	0.77	0.43	0.77	0.77	0.77	0.97	0.76
Na, ueq/l	5.79	13.92	3.44	3.48	0.65	2.61	8.05	6.96	4.31	5.22
Sum	9.80	23.53	14.56	15.03	5.63	10.84	20.45	18.33	14.31	15.75
Acid Anions										
SO_4, ueq/l	19.99	27.89	24.15	41.43	51.63	64.54	40.60	44.76	41.22	55.95
NO_3, ueq/l	12.10	21.78	14.84	25.00	22.42	27.74	23.55	25.32	21.94	30.44
Cl, ueq/l	7.05	16.08	4.80	4.80	3.10	4.51	7.62	7.62	5.36	6.48
Sum	39.14	65.75	43.79	71.23	77.15	96.79	71.77	77.70	68.52	92.87

SOUTH FORK BENS CREEK, PA

	Winter		Spring		Summer		Fall		Annual	
	Dec 83 - Feb 84		Mar 84 - May 84		Jun 84 - Aug 84		Sep 84 - Nov 84		Jan 84 - Dec 84	
	Site	Region	Site	Region	Site	Region	Site	Region	Site	Region
Precipitation, cm	30.00	26.46	42.57	34.69	44.27	37.73	20.52	23.16	123.85	118.98
pH, s.u.	4.09	4.48	4.21	4.30	3.89	4.09	4.45	4.38	4.14	4.24
Base Cations										
Ca, ueq/l	29.44	6.49	17.00	9.48	6.99	6.49	4.49	4.99	13.97	7.48
Mg, ueq/l	4.94	1.65	3.29	3.29	2.47	2.47	4.11	2.47	3.29	2.46
K, ueq/l	4.09	0.51	3.07	0.77	1.53	1.28	1.02	0.51	2.56	1.02
Na, ueq/l	19.14	3.05	8.27	2.18	4.35	2.18	4.35	4.79	7.83	3.04
Sum	57.61	11.70	31.63	15.72	15.34	12.42	13.97	12.76	27.65	14.00
Acid Anions										
SO_4, ueq/l	95.36	31.64	64.54	55.58	119.09	92.02	49.15	42.47	80.57	61.98
NO_3, ueq/l	65.67	22.42	35.71	30.80	39.96	32.26	25.00	20.97	39.35	28.50
Cl, ueq/l	15.23	5.08	7.05	4.23	5.64	4.23	4.80	5.35	7.33	4.79
Sum	176.26	59.14	107.30	90.61	164.69	128.51	78.94	68.79	127.15	95.27

Table 4.1. Continued.

COWEETA (MOSES AND JARRETT CREEKS), NC

	Winter Dec 83 - Feb 84		Spring Mar 84 - May 84		Summer Jun 84 - Aug 84		Fall Sep 84 - Nov 84		Annual Jan 84 - Dec 84	
	Site	Region	Site	Region	Site	Region	Site	Region	Site	Region
Precipitation, cm	60.90	37.00	59.41	39.62	41.76	38.12	34.15	21.03	179.87	132.80
pH, s.u.	4.92	4.76	4.74	4.64	4.26	4.24	4.65	4.60	4.65	4.48
Base Cations										
Ca, ueq/l	2.50	4.49	14.47	11.48	3.49	6.49	2.50	3.49	7.98	7.48
Mg, ueq/l	1.65	1.65	3.04	3.29	1.48	2.47	2.80	3.29	2.63	2.46
K, ueq/l	0.31	0.51	1.28	1.28	1.46	1.02	0.51	1.53	0.92	1.02
Na, ueq/l	5.66	5.22	5.96	6.09	1.91	2.61	9.09	7.40	6.53	5.22
Sum	10.12	11.87	24.75	22.14	8.34	12.59	14.90	15.71	19.06	16.18
Acid Anions										
SO_4, ueq/l	16.45	23.11	35.39	38.72	51.22	58.71	23.73	28.93	30.61	39.31
NO_3, ueq/l	6.13	9.83	13.23	17.10	24.20	22.58	10.00	10.97	12.25	16.28
Cl, ueq/l	6.77	6.77	9.31	7.62	3.39	6.49	9.59	9.31	8.75	7.61
Sum	29.35	39.71	57.93	63.44	78.81	87.78	43.32	49.21	51.61	63.20

SALINE RIVER, AR[1]

	Winter		Spring		Summer		Fall		Annual	
	Site	Region	Site	Region	Site	Region	Site	Region	Site	Region
Precipitation, cm	38.18	27.49	53.11	32.85	27.69	28.64	33.07	53.03	152.05	142.41
pH, s.u.	4.46	4.85	4.87	4.97	4.53	4.59	4.46	4.90	4.58	4.82
Base Cations										
Ca, ueq/l	9.39	7.49	8.65	25.45	16.12	10.97	8.08	3.49	10.29	9.98
Mg, ueq/l	5.01	2.47	2.84	4.94	3.75	3.29	3.49	2.47	3.84	3.29
K, ueq/l	2.82	.51	3.71	2.05	3.08	1.02	6.98	0.77	3.78	1.02
Na, ueq/l	19.35	6.53	8.61	10.88	10.63	5.66	9.71	6.96	13.06	7.83
Sum	36.57	17.00	23.81	43.32	33.58	20.94	28.26	13.69	30.97	22.12
Acid Anions										
SO_4, ueq/l	44.41	24.56	29.49	40.39	33.08	32.27	36.00	17.28	35.83	26.44
NO_3, ueq/l	21.55	11.02	13.93	20.32	18.89	21.93	21.28	8.07	18.18	13.89
Cl, ueq/l	22.16	7.05	7.89	10.03	9.14	6.49	13.76	7.33	13.53	8.46
Sum	88.12	42.63	51.31	70.74	61.11	60.69	71.04	32.68	67.54	48.79

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[1] Site data is from 1985 and region data is from 1984.

Table 4.2. Seasonal trends in wet deposition composition.

Site/(Region)	pH		Base Cations		SO_4		NO_3		Rain	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Biscuit Brook	S (S)	W (W)	W (S)	F (W)	W (W)	S (S)	W (W)	F (S)	F,S (F)	Sp (Sp)
South Fork Bens Creek	S (S)	F (W)	F (W)	W (Sp)	F (W)	S (S)	F (F)	W (S)	F (F)	S,Sp (S)
Coweeta	S (S)	W (W)	W (W)	Sp (Sp)	W (W)	S (S)	W (W)	S (S)	F,S (F)	W,Sp (Sp)
Saline	F,W (S)	Sp (Sp)	Sp (F)	W (Sp)	Sp (F)	W (Sp)	Sp (F)	W (S)	S,F (W)	Sp (F)

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* W = Winter
Sp = Spring
S = Summer
F = Fall
() = Regional seasonal trends

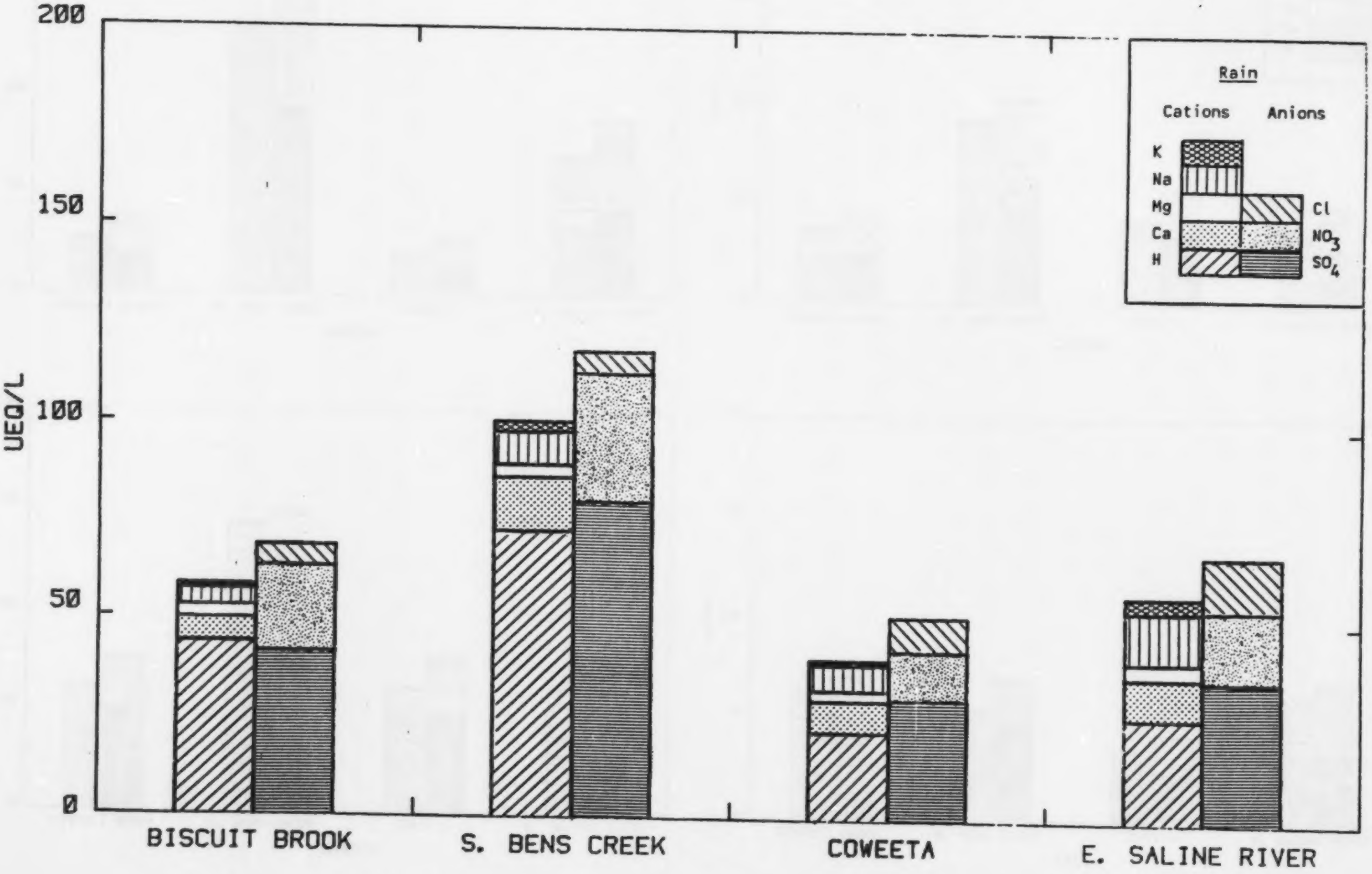

Figure 4.1. Volume-weighted average precipitation chemistry for the study period.

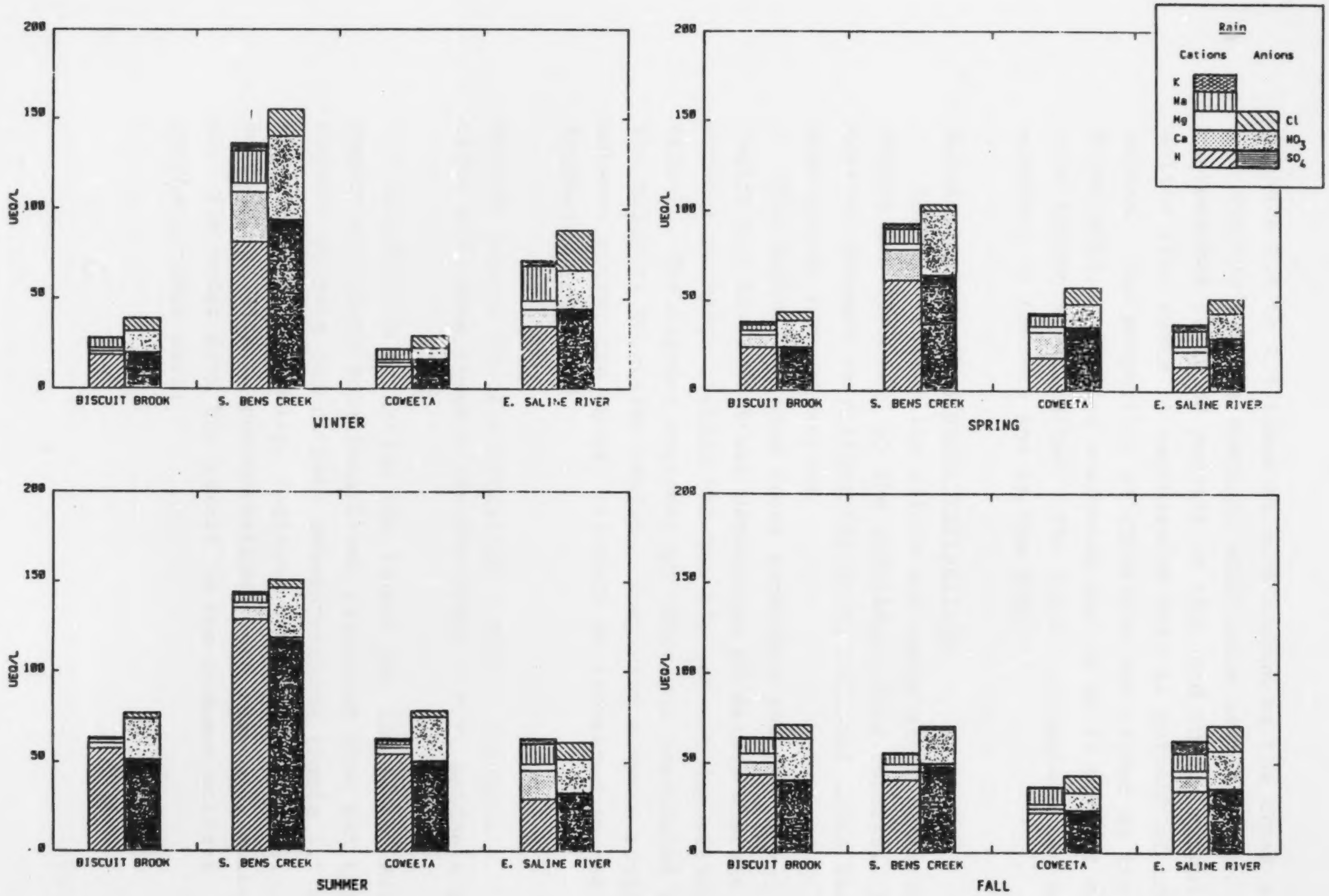

Figure 4.2. Volume-weighted average precipitation chemistry by season.

to have 1.5 to 2.6 times as much sodium as the other regions.

Sulfate was the dominant acid anion at all sites. It represented 60 to 68 percent of the acid anions except at the Saline site where it represented only 54 percent of the acid anions. The proportion of chlorides was higher at the Saline River site. Nitrates accounted for 24 to 33 percent of the acid anions at all sites. The lowest percentage (24 to 26) occurred at Coweeta and in the SBRP.

4.2.2 Spatial (Regional) Variability

Spatial variability within and among study sites in a region are discussed in the individual site reports. This section focuses on differences among regional sites based on mean annual concentrations.

The South Fork Bens Creek watershed and the Laurel Hill region had the lowest wet deposition pH values whereas the Coweeta NADP/NTN station had the highest wet deposition pH values. The highest regional pH value was associated with the Ouachita Mountains region. Comparing between regions and between sites, the annual rainfall pH increased in the following order:

REGION: Laurel Ridge < Catskills < SBRP < Ouachita
SITE: S.F. Bens Creek < Biscuit Brook < E.F. Saline < Coweeta

In addition to having the lowest pH, the Laurel Hill region and South Fork Bens Creek watershed also had the highest sulfate and nitrate concentrations (Table 4.1 and Figure 4.1). Generally, regional and site volume-weighted sulfate and nitrate concentrations were inversely related to pH. The order from the lowest to the highest sulfate concentrations were:

REGION: Ouachita < SBRP < Catskills < Laurel Ridge
SITE: Coweeta < E.F. Saline < Biscuit Brook < S.F. Bens Creek

Nitrate concentrations demonstrated the same trend with one exception; the Catskills region had greater average nitrate concentrations than the Laurel Hill region (Table 4.1).

Wet deposition sulfate concentrations were comparable (i.e., <20% difference) at the East Fork Saline study site and the Coweeta, NC site. The SBRP and Ouachita regions were greater than 30% different for sulfate. In contrast, nitrate concentrations were comparable between the two regions (< 20% difference) but not between the two sites (> 30% difference). Sulfate concentrations at the South Fork Bens Creek were nearly twice as great as at Biscuit Brook but were about equal (i.e., within 10%) on a regional level.

The average annual sulfate to nitrate ratio for the East Fork Saline River and the Biscuit Brook study sites was slightly less than 2:1 (i.e., 1.97:1 and 1.88:1, respectively). These ratios were greater than 2:1 for the South Fork Bens Creek (2.05:1) and Coweeta (2.5:1). The same pattern also held for the regions (i.e., the Ouachita and Catskills regions were less than 2:1 and the SBRP and Laurel Hills were greater than 2:1).

The highest average annual base cation concentrations occurred at the East Fork Saline River site and within the Ouachita region (Table 4.1). Comparing between sites and regions, the order of increasing annual average base cation concentrations was:

REGION: Laurel Ridge < Catskills < SBRP < Ouachitas
SITE: Biscuit Brook < Coweeta < S.F. Bens Creek < E.F. Saline

4.2.3 Seasonal Variability

Wet deposition chemistry varied seasonally among regions (Figure 4.2). The seasonal maximum and minimum average wet deposition constituent concentrations are summarized in Table 4.2.

The minimum seasonal average pH value generally occurred during the summer at the study sites and among the regions. The minimum pH at the Saline study site, however, occurred during the fall and winter (Table 4.2). The maximum seasonal average pH values for the regions usually occurred during the winter but there was greater seasonal variability among study sites related to maximum pH values. The winter season had the highest average pH values in the Biscuit Brook and Coweeta watersheds with the fall and spring seasons having higher average pH values in the South Fork Bens Creek and East Fork Saline watersheds, respectively.

The seasons with minimum and maximum average pH values were inversely correlated with the seasons having the maximum and minimum average sulfate concentrations (Table 4.2). The highest average sulfate concentrations occurred during the summer in the study watersheds and regions with the exception of the East Fork Saline watershed. The highest average sulfate concentration in the Saline watershed occurred during the winter. The lowest average sulfate concentrations also were correlated with maximum seasonal average pH values: Winter in Biscuit Brook and Coweeta watersheds, fall and spring in the South Fork Bens Creek and East Fork Saline watersheds, respectively.

Maximum and minimum average nitrate concentrations were more variable than sulfate concentrations for specific watersheds (Figure 4.2) but were relatively consistent among regions (Table 4.2). At the regional level, the seasonal maximum average nitrate concentrations correlated with seasonal maximum sulfate concentrations; maximum average concentrations of both occurred during the summer. Minimum average nitrate concentrations also occurred during similar seasons as minimum sulfate concentrations. Minimum average nitrate concentrations occurred during winter in the

Catskills and SBRP and during the fall in the Laurel Hill region and Ouachita Mountains. The relative changes in sulfate and nitrate concentrations, however, were different among seasons and among regions. During the summer, for example, the regional sulfate:nitrate ratio ranged from about 1.5 in the Ouachitas to 2.8 in Laurel Hills. This summer ratio was as high as 4.3 in the South Fork Bens Creek, PA, watershed. During the winter, the sulfate:nitrate ratio ranged from 1.3 in the Catskills to 2.4 in the SBRP.

Base cations also varied seasonally (Figure 4.2). The maximum average calcium concentrations occurred during both the spring and fall at Biscuit Brook, during the winter and spring at the South Fork Bens Creek, during the spring at Coweeta, and during the summer at the Saline watershed. Average sodium concentrations were significantly higher during the winter in both the South Fork Bens Creek and Saline watersheds.

4.3 BASEFLOW STREAM CHEMISTRY

Stream chemistry represents the integrated response of the watershed and stream processes to many factors including acidic deposition. This section will discuss seasonal differences in stream chemistry at stream baseflow (i.e., non-event). All stream values are flow-weighted averages and are summarized in Table 4.3 and Figures 4.3 - 4.7.

ANC concentrations in North and South Fork Bens Creeks are difficult to compare to ANC data from the other sites because a different analytical method was used (See Section 3.4). ANC was reported as $CaCO_3$ alkalinity but only down to 0.5 mg/l $CaCO_3$ (10 ueq/l). This had the resultant effect of yielding overestimates of flow-weighted ANC values (See Tables 4.3, 4.5, 4.6, and 4.11 and Figures 4.3-4.7). These, in turn, result in poor cation/anion balances for those computations.

Table 4.3. Annual flow-weighted streamflow composition.

	Biscuit Brook	South Fork Bens Creek	North Fork Bens Creek	Jarrett Creek	Moses Creek	East Fork Saline
pH, s.u.	6.0	6.2	5.4	6.8	7.1	6.6
Base Cations						
Ca, ueq/l	123.7	167.5	160.0	42.9	63.7	33.6
Mg, ueq/l	45.1	84.4	76.8	34.9	40.4	43.3
K, ueq/l	5.5	18.7	15.7	10.9	14.6	12.4
Na, ueq/l	17.5	23.1	61.3	50.6	59.1	44.1
Sum, ueq/l	191.8	293.7	313.8	139.3	177.8	133.4
Al, ug/l	69.3	48.6	101.6	30.6	36.9	27.0
Major Anions plus ANC						
ANC, ueq/l	15.5	78.6	43.1	68.0	135.9	58.8
SO_4, ueq/l	138.4	190.3	206.3	18.2	22.0	54.1
NO_3, ueq/l	20.2	52.2	46.4	1.3	1.0	2.4
Cl, ueq/l	17.7	27.2	83.4	32.3	15.3	36.4
Sum, ueq/l	191.8	348.3	379.2	119.8	174.2	151.7

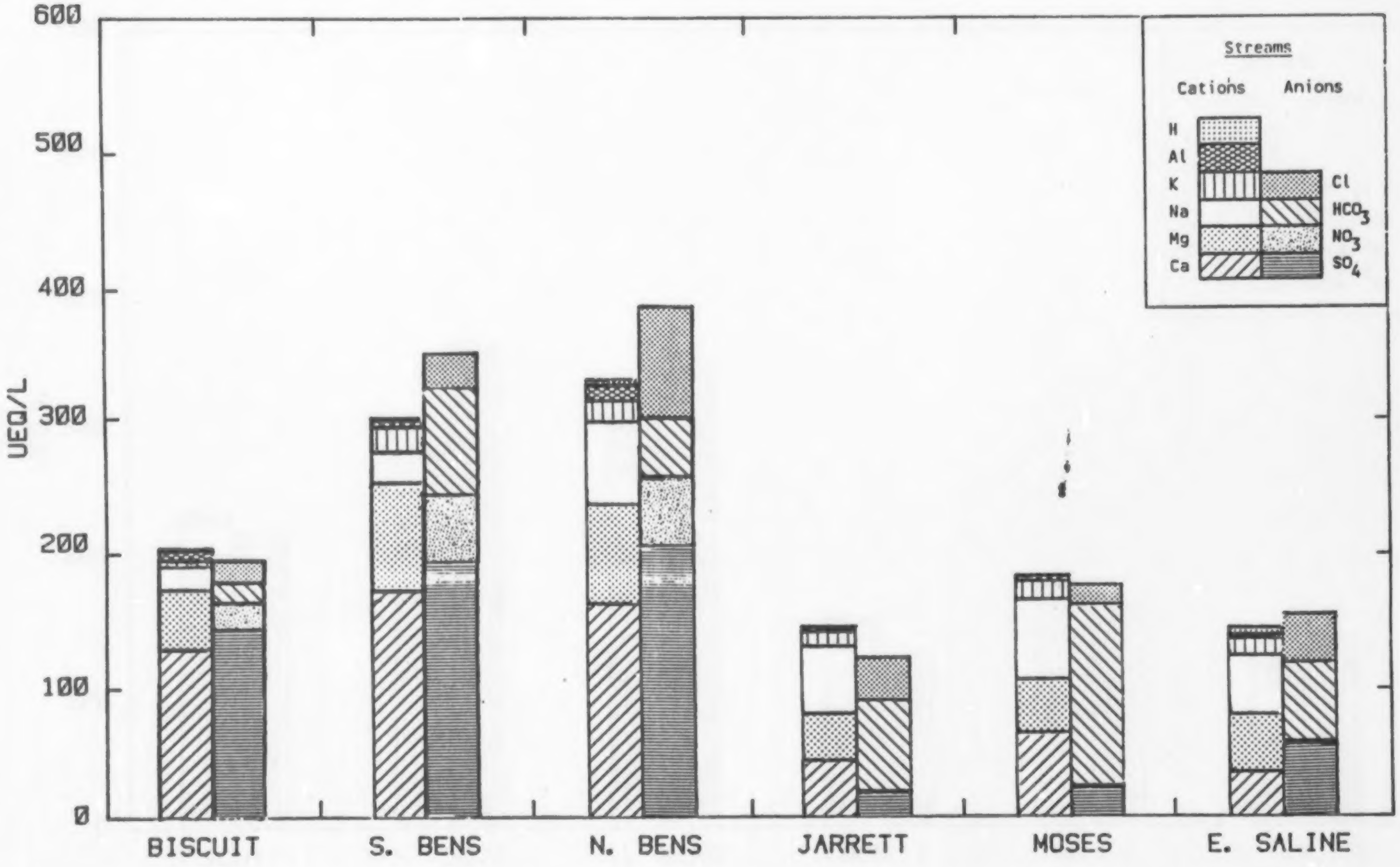

Figure 4.3. Flow-weighted average stream chemistry for the study period.

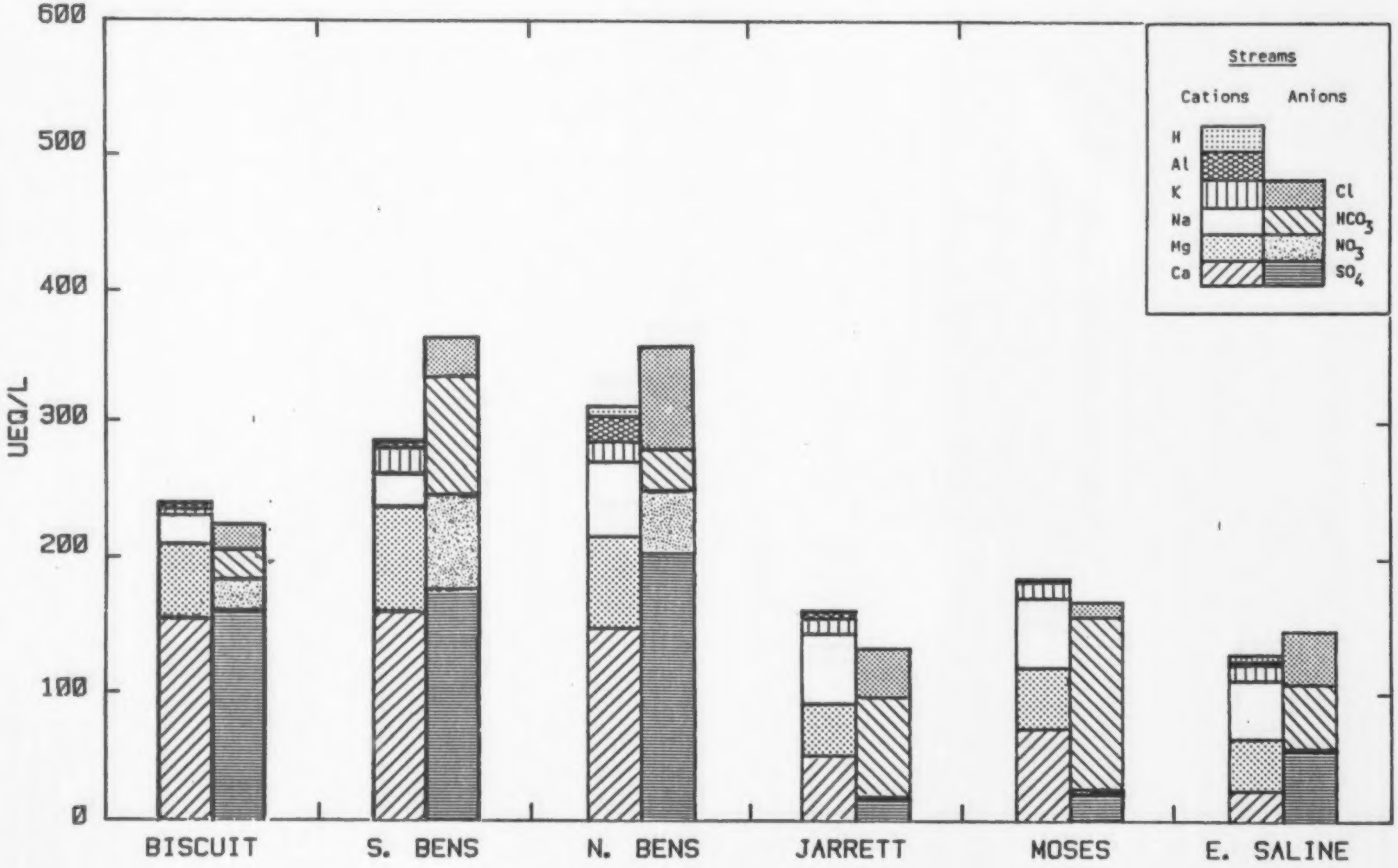

Figure 4.4. Flow-weighted average stream chemistry for the winter period.

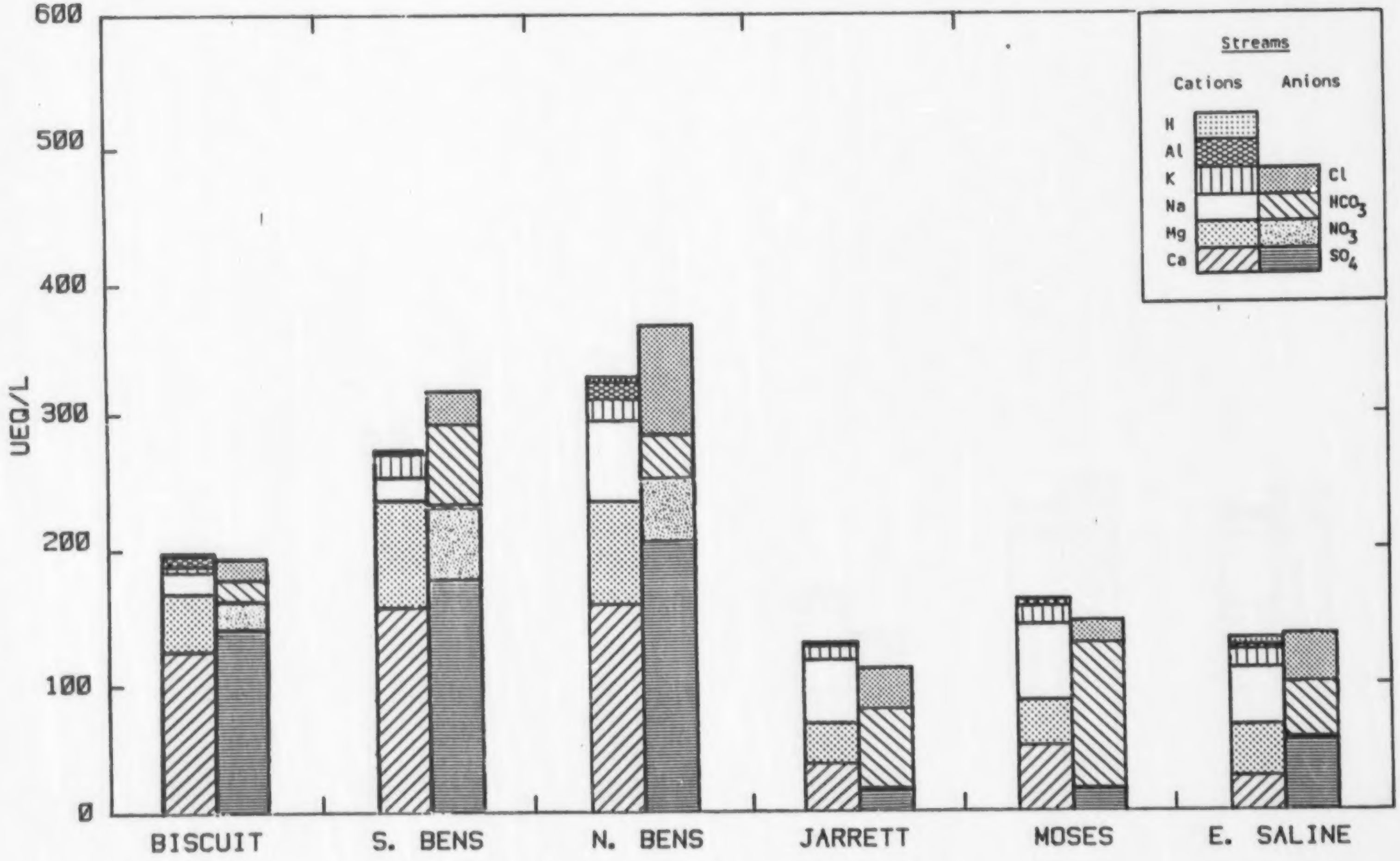

Figure 4.5. Flow-weighted average stream chemistry for the spring period.

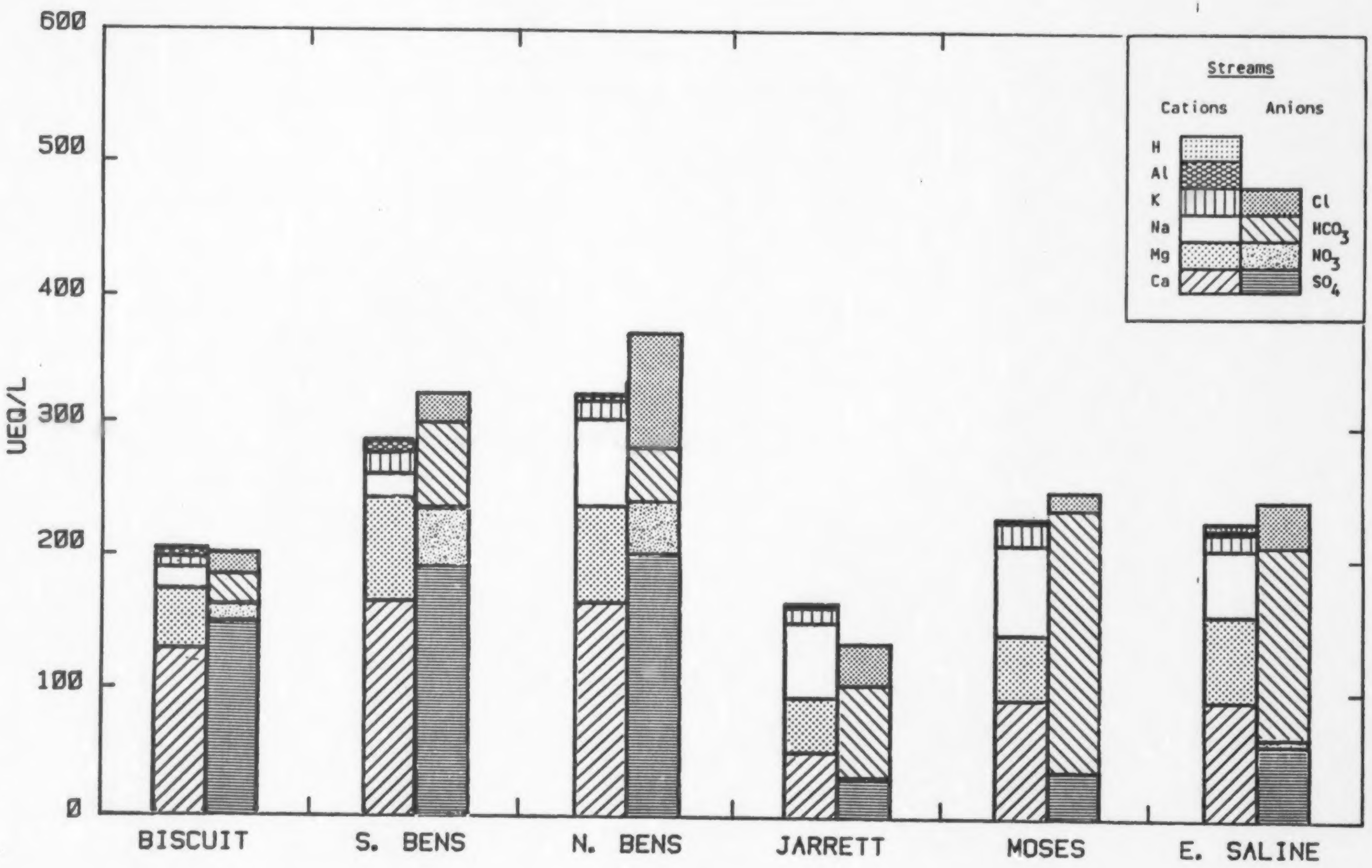

Figure 4.6. Flow-weighted average stream chemistry for the summer period.

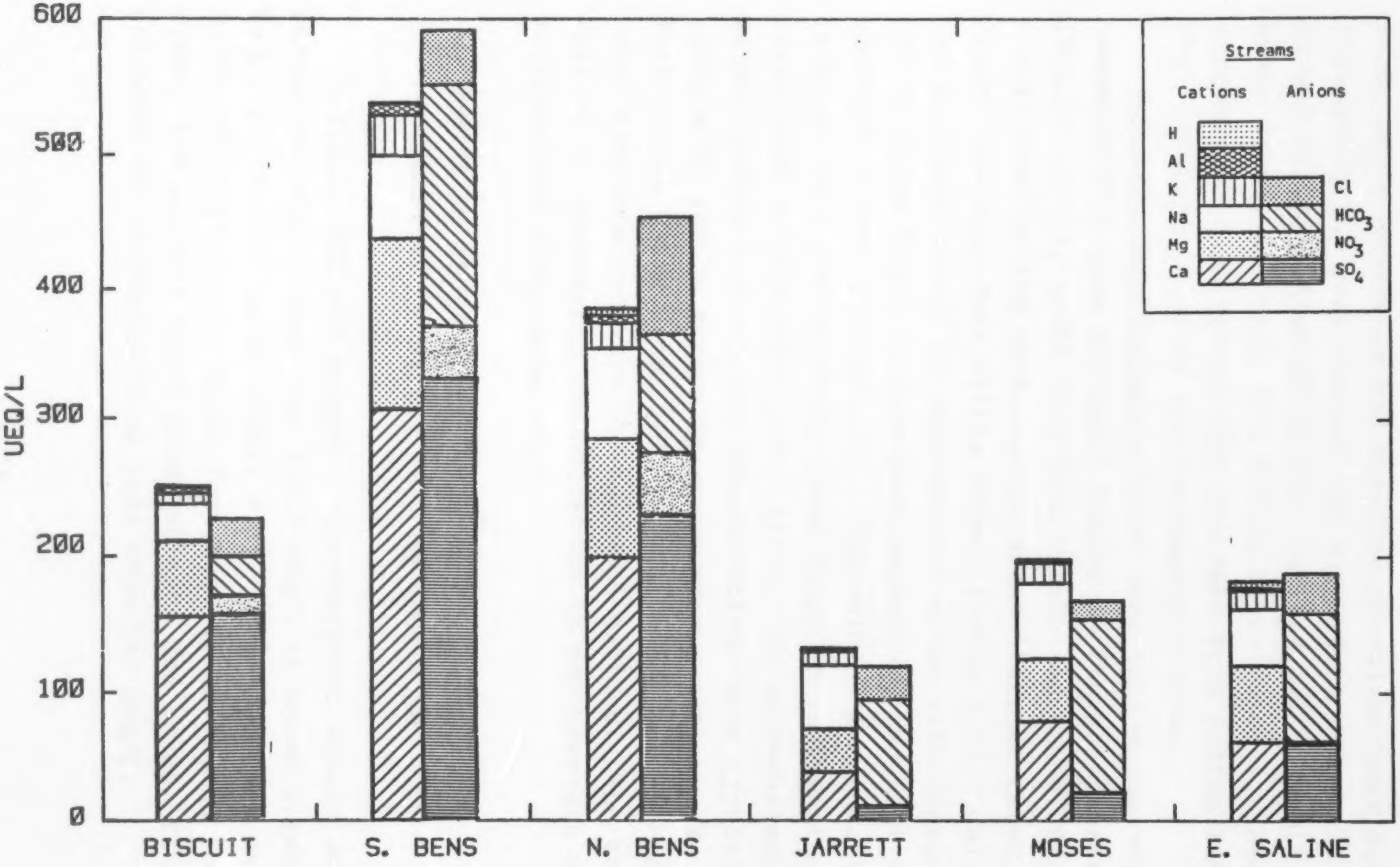

Figure 4.7. Flow-weighted average stream chemistry for the fall period.

4.3.1 Site Variation (Annual)

4.3.1.1 pH - Biscuit Brook and South Fork Bens Creek study sites generally had baseflow pH values near 6.0 throughout the year whereas the North Fork Bens Creek had the lowest flow-weighted pH of 5.4 (Table 4.3). Jarrett Creek, Moses Creek, and East Fork Saline River generally had circumneutral pH values with the East Fork Saline site having the lowest pH (6.6) of the southeastern sites.

4.3.1.2 Base Cations - Total base cation concentrations averaged more than 115 ueq/l higher in the northeasern sites (Biscuit Brook, South Fork Bens Creek, and North Fork Bens Creek) than in the southeastern sites (Jarrett Creek, Moses Creek, and East Fork Saline River) (Table 4.3). Calcium was the dominant cation in northeastern sites with concentrations two to three times greater than magnesium, the next most abundant cation (Figure 4.3). The calcium concentrations, in general, were two to three times lower in southeastern study sites than northeastern study sites. In southeastern study sites, sodium and calcium concentrations were approximately equal with sodium typically the dominant cation. In the East Fork Saline River watershed, magnesium and sodium had similar concentrations and were the dominant cations. The dominant cations in increasing concentration in northeastern and southeastern study areas were:

NORTHEAST STUDY SITES: $K < Na < Mg < Ca$
SOUTHEAST STUDY SITES: $K < Mg < Ca < Na$

4.3.1.3 ANC and Anions - Flow-weighted annual ANC concentrations ranged from 135.9 ueq/l at Moses Creek to 15.5 ueq/l at Biscuit Brook (Table 4.3). The East Fork Saline River, Biscuit Brook, South Fork Bens Creek, North Fork Bens Creek, and Jarrett Creek study streams had annual flow-weighted ANC concentrations less than 100 ueq/l.

Annual flow-weighted sulfate and nitrate concentrations at the northeastern study sites were about an order of magnitude higher than at the southeastern study sites (Table 4.3 and Figure 4.3). Sulfate was the dominant anion in the Biscuit Brook, South Fork Bens Creek, and North Fork Bens Creek study sites. Sulfate concentrations in these study sites were consistently greater than ANC concentrations. ANC concentrations were greater than the sulfate concentrations at all the southeastern sites. Sulfate concentrations were greater than either chloride or nitrate concentrations in all the study areas except Jarrett Creek where chloride concentrations were greater than sulfate and nitrate concentrations.

4.3.1.4 Dissolved Aluminum - Dissolved aluminum concentrations ranged from 27 ug/l at the East Fork Saline site to 101.6 ug/l at the North Fork Bens Creek site (Table 4.3). North Fork Bens Creek had the highest flow-weighted concentration (101.6 ug/l), which is consistent with its lower pH (5.4).

4.3.2 Seasonal Variability

4.3.2.1 pH - Maximum flow-weighted stream pH generally occurred in the summer and fall in all streams except Jarrett Creek where it occurred in the winter (Tables 4.4 - 4.9). Minimum flow-weighted stream pH occurred during the spring and winter at the study sites.

4.3.2.2 Base Cations - Maximum average base cation concentrations generally occurred during the fall in the northeastern streams (i.e. Biscuit Brook, North and South Fork Bens Creek) and during the summer in the southeastern streams (i.e., Moses and Jarrett Creek, East Fork Saline) (Tables 4.4 - 4.9 and Figures 4.4 - 4.7). The minimum base cation concentrations occurred during the spring, except in the East Fork Saline River and North Fork Bens Creek where minimum concentrations occurred in the winter. Calcium

Table 4.4. Flow-weighted seasonal streamflow composition for Biscuit Brook (Oct 83 - Sep 84).

	Winter	Spring	Summer	Fall	Annual
pH, s.u.	6.3	5.9	6.3	6.4	6.0
Base Cations					
Ca, ueq/l	148.9	119.7	124.6	150.5	123.7
Mg, ueq/l	56.9	43.3	45.6	57.1	45.1
K, ueq/l	4.8	5.1	8.4	7.7	5.5
Na, ueq/l	21.8	16.2	16.2	27.9	17.5
Sum, ueq/l	232.4	184.3	194.8	243.2	191.8
Al, ug/l	41.4	73.7	60.3	43.2	69.3
Major Anions plus ANC					
ANC, ueq/l	22.7	13.3	23.5	29.2	15.5
SO_4, ueq/l	155.4	135.9	145.1	152.4	138.4
NO_3, ueq/l	23.3	21.1	13.3	13.7	20.2
Cl, ueq/l	19.9	16.4	16.5	29.2	17.7
Sum, ueq/l	221.3	186.7	198.4	224.5	191.8

Table 4.5. Flow-weighted seasonal streamflow composition for South Fork Bens Creek (Oct 83 - Sep 84).

	Winter	Spring	Summer	Fall	Annual
pH, s.u.	6.2	6.2	6.2	6.4	6.2
Base Cations					
Ca, ueq/l	155.4	152.3	161.6	306.2	167.5
Mg, ueq/l	79.9	81.5	80.3	129.6	84.4
K, ueq/l	18.9	17.6	16.5	30.1	18.7
Na, ueq/l	24.7	17.4	17.4	61.9	23.1
Sum, ueq/l	278.8	268.8	275.8	527.8	293.7
Al, ug/l	44.1	19.8	83.6	80.9	48.6
Major Anions plus ANC					
ANC, ueq/l	86.9	59.9	64.0	182.3	78.6
SO_4, ueq/l	175.2	173.6	189.4	331.1	190.3
NO_3, ueq/l	71.2	55.2	45.3	39.1	52.2
Cl, ueq/l	30.5	24.8	22.6	40.9	27.2
Sum, ueq/l	363.8	313.5	321.3	593.4	348.3

Table 4.6. Flow-weighted seasonal streamflow composition for North Fork Bens Creek (Oct 83 - Sep 84).

	Winter	Spring	Summer	Fall	Annual
pH, s.u.	5.2	5.4	5.9	5.8	5.4
Base Cations					
Ca, ueq/l	144.4	156.9	162.6	197.1	160.0
Mg, ueq/l	70.6	77.4	74.7	88.0	76.8
K, ueq/l	15.2	15.9	13.5	18.6	15.7
Na, ueq/l	55.3	60.6	66.5	66.7	61.3
Sum, ueq/l	285.5	310.8	317.3	370.4	313.8
Al, ug/l	165.5	110.6	38.7	52.2	101.6
Major Anions plus ANC					
ANC, ueq/l	30.4	32.5	40.6	88.7	43.1
SO_4, ueq/l	201.8	205.2	199.5	229.3	206.3
NO_3, ueq/l	46.5	47.9	40.9	44.8	46.4
Cl, ueq/l	77.1	82.4	89.1	89.6	83.4
Sum, ueq/l	355.8	368.0	370.1	452.4	379.2

Table 4.7. Flow-weighted seasonal streamflow composition for Jarrett Creek (May 84 - Mar 85).

	Winter	Spring	Summer	Fall	Annual
pH, s.u.	6.9	6.7	6.8	6.8	6.8
Base Cations					
Ca, ueq/l	49.9	36.4	49.9	36.9	42.9
Mg, ueq/l	38.7	30.5	41.2	32.1	34.9
K, ueq/l	11.5	10.2	12.0	10.0	10.9
Na, ueq/l	52.2	47.9	56.6	47.9	50.6
Sum, ueq/l	152.3	125.0	159.7	126.9	139.3
Al, ug/l	50.4	19.8	26.1	19.8	30.6
Major Anions plus ANC					
ANC, ueq/l	75.0	60.0	70.0	80.0	68.0
SO_4, ueq/l	16.6	16.6	29.1	10.4	18.2
NO_3, ueq/l	1.6	1.0	1.6	0.6	1.3
Cl, ueq/l	36.7	31.0	31.0	25.4	32.3
Sum, ueq/l	129.9	108.6	131.7	116.4	119.8

Table 4.8. Flow-weighted seasonal streamflow composition for Moses Creek (May 84 - Mar 85).

	Winter	Spring	Summer	Fall	Annual
pH, s.u.	6.8	6.8	7.0	7.3	7.1
Base Cations					
Ca, ueq/l	69.9	49.9	89.8	74.9	63.7
Mg, ueq/l	46.1	34.6	49.4	46.9	40.4
K, ueq/l	12.5	13.6	18.2	15.4	14.6
Na, ueq/l	52.2	56.6	69.6	56.6	59.1
Sum, ueq/l	180.7	154.7	227.0	193.8	177.8
Al, ug/l	19.8	50.4	19.8	19.8	36.9
Major Anions plus ANC					
ANC, ueq/l	130.0	110.0	200.0	130.0	135.9
SO_4, ueq/l	20.8	16.6	35.4	20.8	22.0
NO_3, ueq/l	3.2	0.6	0.6	0.6	1.0
Cl, ueq/l	11.3	16.9	14.1	14.1	15.3
Sum, ueq/l	165.3	144.1	250.1	165.5	174.2

Table 4.9. Flow-weighted seasonal streamflow composition for East Fork Saline (Nov 84 - Oct 85).

	Winter	Spring	Summer	Fall	Annual
pH, s.u.	6.5	6.5	7.0	6.9	6.6
Base Cations					
Ca, ueq/l	23.1	26.0	89.7	59.0	33.6
Mg, ueq/l	39.4	38.9	64.9	57.3	43.3
K, ueq/l	11.1	13.1	12.6	13.9	12.4
Na, ueq/l	44.0	43.5	51.7	42.3	44.1
Sum, ueq/l	117.6	121.5	218.9	172.5	133.4
Al, ug/l	26.1	32.4	27.0	18.9	27.0
Major Anions plus ANC					
ANC, ueq/l	48.1	41.8	146.8	96.2	58.8
SO_4, ueq/l	53.8	53.1	56.4	56.8	54.1
NO_3, ueq/l	1.8	2.5	5.4	2.2	2.4
Cl, ueq/l	39.1	36.1	34.7	30.2	36.4
Sum, ueq/l	142.8	133.5	243.3	185.4	151.7

concentrations followed the same trend. The rest of the cation constituents demonstrated more variability. For example, minimum sodium concentrations occurred in the spring and summer at Biscuit Brook and South Fork Bens Creek, in the winter at North Fork Bens Creek and Moses Creek, in the spring and fall at Jarrett Creek, and in the fall at East Fork Saline River.

4.3.2.3 ANC and Anions - ANC concentrations generally were highest during the fall and/or winter period at the Biscuit Brook, North and South Fork Bens Creeks, and Jarrett Creek study sites and during the summer period at the Moses Creek and East Fork Saline study sites (Tables 4.4 - 4.9). Minimum flow-weighted ANC concentrations occurred in the spring at all sites except North Fork Bens Creek where it occurred during the spring and winter.

Maximum and minimum sulfate concentrations generally corresponded with the seasonal maxima and minima in base cations, respectively (Tables 4.4 - 4.9 and Figures 4.4 - 4.7). Maximum flow-weighted nitrate concentrations occurred during the winter at all sites except North Fork Bens Creek. Maximum flow-weighted nitrate concentrations were the same at Jarrett Creek in the winter and summer (Table 4.7). Minimum flow-weighted nitrate concentrations generally occurred during the summer at the Biscuit Brook and North Fork Bens Creek sites, during the fall at the South Fork Bens Creek, East Fork Saline, and Jarrett Creek sites, and during the spring, summer, and fall at Moses Creek site. Maximum flow-weighted chloride concentrations occurred during the winter at the East Fork Saline and Jarrett Creek sites, during the fall at the Biscuit Brook and South and North Fork Bens Creek sites, and during the spring at the Moses Creek site.

4.3.2.4 Dissolved Aluminum - Dissolved aluminum concentrations increased slightly in North Fork Bens Creek during the winter and early spring in association with pH values less than 5.5 (Table 4.6). Aluminum concentrations were comparable and low (i.e. < 85.4 ug/l) in the other streams in all regions. The highest dissolved aluminum concentrations occurrred during the spring in Biscuit Brook, Moses Creek, and East Fork Saline River. In North Fork Bens Creek and Jarrett Creek, the highest dissolved aluminum concentrations occurred in the winter. Only in South Fork Bens Creek did the highest concentrations occur in the summer.

4.3.2.5 Comparison - The seasons during which various constituents were at the minimum and maximum concentrations are summarized in Table 4.10. In those cases where more than one season is listed, there were no real differences among the seasonal values. The first season listed is the season with the absolute minimum or maximum.

Minimum flow-weighted pH values occurred in the winter and/or spring at all sites. Maximum flow-weighted pH values occurred during all seasons except the spring. Minimum flow-weighted base cation and ANC concentrations occurred during the winter and spring at all sites. Maximum ANC concentrations occurred in the fall in the northeastern sites and in the summer in the southeastern sites except for Jarrett Creek where maximum ANC concentrations occurred in the fall. Average maximum sulfate concentrations occurred in the fall or summer except for Biscuit Brook where it occurred in the winter. Maximum flow-weighted nitrate concentrations occurred in the winter at all sites except North Fork Bens Creek, where the maximum occurred during the spring.

4.4 EPISODES

Episodes were defined as a subset of hydrologic events based on acidification occurring during the hydrometeorological event. Episodes can occur in response to snowmelt or rainfall. This section discusses: the chemical changes occurring during a typical storm event at each site; snowmelt

Table 4.10. Seasonal trends in stream chemistry.

Study Site	pH		Base Cations		ANC		SO_4		NO_3	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Biscuit Brook	Sp*	F	Sp	F	Sp	F	Sp	W	S	W
North Fork Bens Creek	W	S	W	F	W,Sp	F	S	F	S #	Sp
South Fork Bens Creek	W,Sp S #	F	Sp	F	Sp	F	Sp	F	F	W
Jarrett Creek	Sp #	W	Sp #	S	Sp	F	F	S	F	S,W
Moses Creek	W,Sp	F	Sp	S	Sp	S	Sp	S	Sp,S, F	W
East Fork Saline River	Sp,W	S	W	S	Sp	S	Sp #	F	F	W

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* W = Winter
Sp = Spring
S = Summer
F = Fall

# No significant pattern among seasons

episodes in the Northeast; and storm episodes at all six sites. A summary of the episodes based on precipitation input, peak discharge, pH and ANC minima, hydrogen ion concentration maxima, and change in pH, hydrogen ion concentration, and ANC at each site is given in Table 4.11.

4.4.1 Snowmelt Episodes

Snowmelt episodes were monitored from 23-26 February 1985 (Table 4.11, Figure 4.8) and 11-13 March 1985 in Biscuit Brook (Figure 4.9) and from 22-28 February 1985 in North Fork Bens Creek (Figure 4.10).

Snowmelt durations for the episodes monitored at Biscuit Brook were about 75 hr in February 1985 and at least 40 hr in March 1985. At North Fork Bens Creek, the snowmelt episodes lasted about 160 hr.

The February snowmelt event in Biscuit Brook resulted in a double peaked hydrograph with increased pH during the first peak and the minimum pH (4.89) recorded near the maximum discharge during the second peak (Figure 4.8). On 11-13 March 1985, the snowmelt event resulted in a single peaked hydrograph with the minimum pH value of 5.45 occurring after the peak discharge (Figure 4-9). A second pH minimum (5.47) occurred near the end of the event. Maximum pH depressions for the February and March events were 1.0 and 0.8 units, respectively (Table 4.11). There was a small increase in discharge in North Fork Bens Creek followed by a sustained increase in discharge and a relatively well defined hydrograph (Figure 4.10). The minimum pH (5.23) lagged the peak discharge and occurred on the receding limb of the snowmelt hydrograph. The maximum pH depression was 0.8.

Except for 2 very large storms (See Table 4.11), hydrogen ion concentrations were generally greatest during snowmelt events. During the February and March events at Biscuit Brook the maximum hydrogen ion concentrations were 3.95 and 3.52 ueq/l, respectively, and the changes in hydrogen ion

Table 4.11. Summary of episodes.

BISCUIT BROOK

Dates	Precip (cm)	Peak Flow (m^3/s)	pH Min.	Δ pH	Max. H^+ (ueq/l)	Δ H^+	ANC Min. (ueq/l)	Δ ANC (ueq/l)
Apr 10-11, 1983	-	2.92	5.18	0.62	6.56	4.98	1.0	25.0
Nov 10-11, 1983	4.06	0.19	6.18	0.22	0.66	0.26	34.0	2.0
Mar 21, 1984	4.83*	0.79	5.89	0.32	1.29	0.67	14.0	4.0
Apr 3-6, 1984	5.95*	18.58	4.89	1.28	12.78	12.1	-12.0	32.0
Nov 5, 1984	2.21	0.17	6.10	0.14	0.79	0.22	31.8	25.0
Feb 23-26, 1985	3.56*	2.32	5.40	1.00	3.95	3.55	6.8	29.2
Mar 11-13, 1985	0.38*	2.38	5.45	0.83	3.52	3.00	4.0	32.0
May 17-21, 1985	3.30	0.71	6.02	0.38	0.95	0.55	20.0	22.0
Jul 31, 1985	1.83	1.08	6.06	0.84	0.86	0.74	24.0	14.0
Sep 26-28, 1985	17.37	21.14	4.90	1.71	12.49	12.25	-14.0	64.0

NORTH FORK BENS CREEK

Dates	Precip (cm)	Peak Flow (m^3/s)	pH Min.	Δ pH	Max. H^+ (ueq/l)	Δ H^+	ANC[2] Min. (ueq/l)	Δ ANC[2] (ueq/l)
Dec 19-21, 1984	2.16	0.64	5.36	0.3	4.33	2.16	20	$0^{\#}$
Feb 22-28, 1985	*	2.10	5.23	0.8	5.84	4.92	20	$0^{\#}$
Mar 12-13, 1985	2.77	0.51	5.30	0.5	4.97	3.40	10	28
May 2-4, 1985	5.84	1.46	5.19	0.7	6.41	5.13	10	$0^{\#}$
Jul 8, 1985	0.18	0.45	5.9	0.6	1.25	0.94	10	10

Table 4.11. Continued.

SOUTH FORK BENS CREEK

Dates	Precip (cm)	Peak Flow (m^3/s)	pH Min.	ΔpH	Max. H^+ (ueq/l)	ΔH^+	ANC^2 Min. (ueq/l)	ΔANC^2 (ueq/l)
Apr 4-6, 1984	7.10	5.21	5.2	0.7	6.26	5.01	40	20
Jun 17-20, 1984	6.73	1.04	6.21	0.6	0.61	0.46	60	40
Aug 13-15, 1984	6.15	1.67	5.7	0.4	1.98	1.19	60	20
Mar 29-31, 1985	8.49	2.72	5.1	1.1	7.88	7.25	10	12

JARRETT CREEK

Dates	Precip (cm)	Peak Flow (m^3/s)	pH Min.	ΔpH	Max. H^+ (ueq/l)	ΔH^+	ANC^1 Min. (ueq/l)	ΔANC^1 (ueq/l)
Nov 28-29, 1984	3.84	4.77	6.07	1.0	0.84	0.76	30	20
Feb 1-2, 1985	3.94	3.40	5.70	0.37	1.98	1.14	30	10

MOSES CREEK

Dates	Precip (cm)	Peak Flow (m^3/s)	pH Min.	ΔpH	Max. H^+ (ueq/l)	ΔH^+	ANC^1 Min. (ueq/l)	ΔANC^1 (ueq/l)
Aug 13-14, 1984	1.91	0.98	6.70	0.11	0.20	0.04	120	60
Nov 28, 1984	0.89	1.32	6.82	0.15	0.15	0.04	80	60
Apr 5-6, 1985	2.24	0.95	6.99	0.05	0.10	0.01	110	30

Table 4.11. Continued.

EAST FORK SALINE RIVER

Dates	Precip (cm)	Peak Flow (m^3/s)	pH Min.	Δ pH	Max. H^+ (ueq/l)	Δ H^+	ANC Min. (ueq/l)	Δ ANC (ueq/l)
Oct 16-17, 1984	4.19	1.02	6.16	0.25	0.69	0.30	32.7	15.0
Dec 13-17, 1984	3.81	1.76	6.17	0.51	0.67	0.46	24.3	49.6
Feb 20-25, 1985	9.14	4.35	6.12	0.7	0.75	0.60	13.0	58.0
Mar 19-22, 1985	6.35	2.22	6.14	0.49	0.72	0.49	22.0	40.2
Aug 5, 1985	1.27	0.05	6.96	0.08	0.11	0.02	134.9	21.8
Sep 13-14, 1985	2.79	0.05	7.09	0.14	0.08	0.02	123.4	142.1
Oct 18-20, 1985	4.06	0.13	6.66	0.26	0.22	0.10	70.2	76.3
Dec 10-12, 1985	6.60	2.85	6.08	0.7	0.83	0.66	0.4	65.6

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* Snowmelt event or combination rainfall/snowmelt event.

# Undetectable difference.

- No precipitation data.

[1] Alkalinity measured as mg/l $CaCO_3$ and converted to ueq/l ANC.

[2] ANC reported to nearest 10 ueq/l.

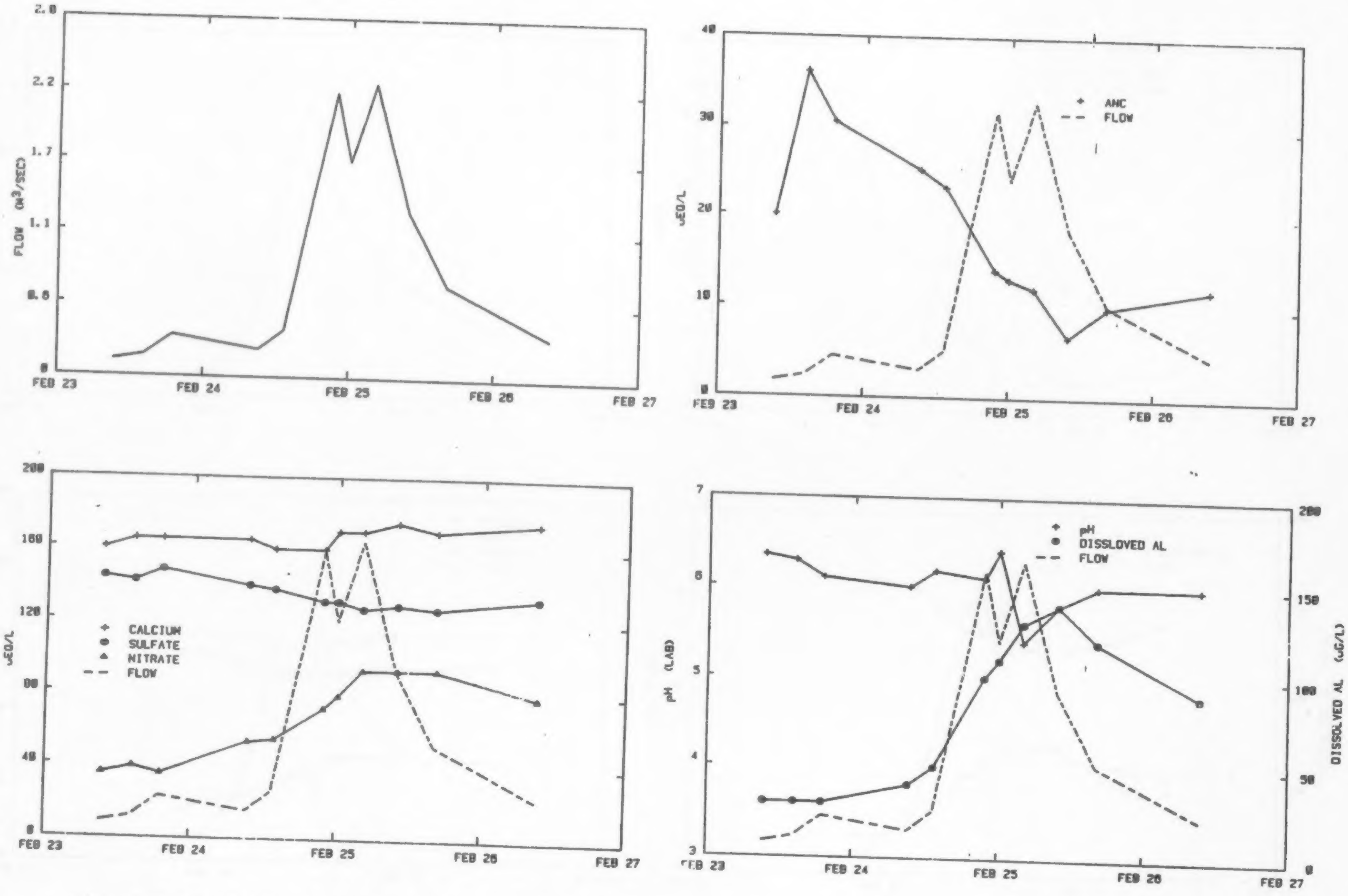

Figure 4.8. Selected variables from a snowmelt event on Biscuit Brook, NY - February 1985.

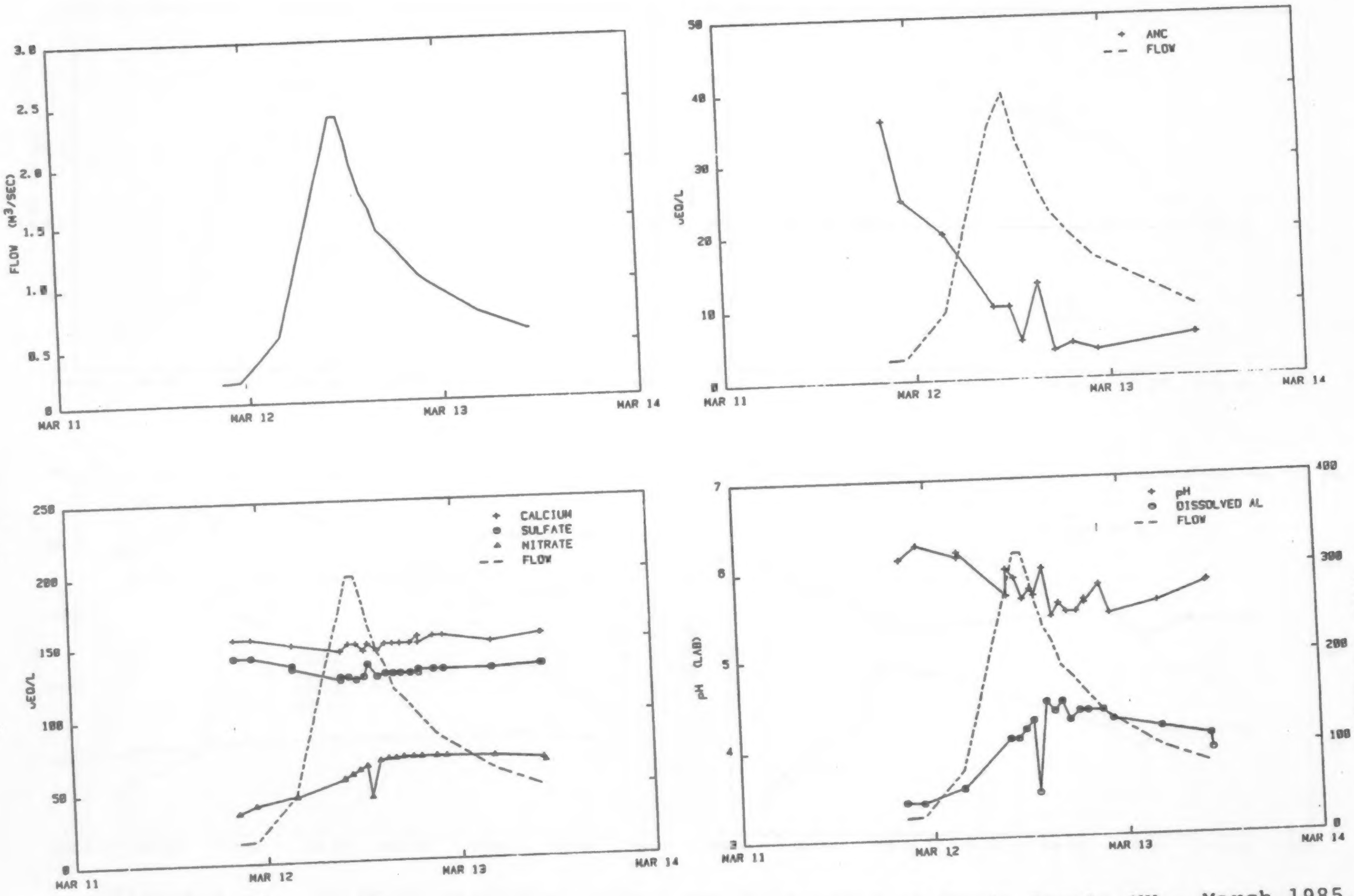

Figure 4.9. Selected variables from a snowmelt event on Biscuit Brook, NY - March 1985.

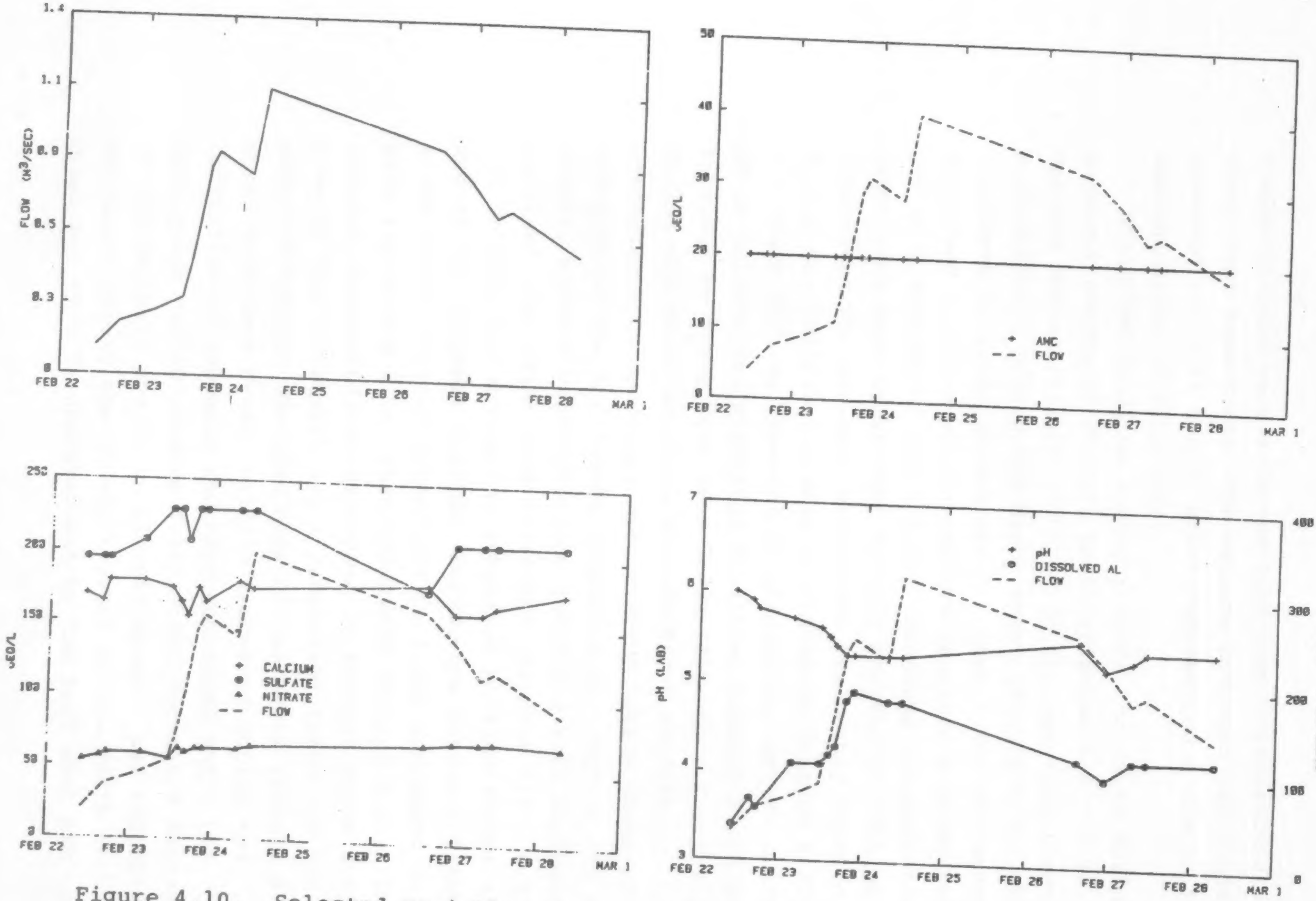

Figure 4.10. Selected variables from a snowmelt event on North Fork Bens Creek, PA - 1985.

concentrations were 3.55 and 3.00 ueq/l, respectively. At North Fork Bens Creek, the maximum hydrogen ion concentration observed was 5.84 ueq/l, which represented a change in concentration of 4.92 ueq/l.

Dissolved aluminum concentrations increased during both snowmelt events at Biscuit Brook (Figures 4.8 - 4.9). Maximum concentrations occurred on the receding limbs of the hydrographs. During the March event (Figure 4.9), aluminum increases followed pH decreases. Except for one measurement, dissolved aluminum concentrations remained greater than 100 ug/l throughout the events. Aluminum concentrations in North Fork Bens Creek were closely correlated with pH throughout the snowmelt period and reasonably related to flow during the initial increase in discharge (Figure 4.10).

There were no apparent relationships between sulfate and pH or sulfate and discharge in either Biscuit Brook in February or North Fork Bens Creek (Figures 4.8 and 4.10). During the March event in Biscuit Brook sulfate concentrations decreased with minimum levels observed during the peak of the hydrograph (Figure 4.9). During all snowmelt events, nitrate concentrations increased with discharge and remained high after flow decreased (Figures 4.8 - 4.10).

Calcium concentrations exhibited no significant trends in any of the snowmelt events. During the February Biscuit Brook event, calcium concentration first decreased slightly with increasing flow, then increased (Figure 4.8). In March, calcium concentrations decreased in Biscuit Brook during the rise of the hydrograph but a consistent trend was not observed through the remainder of the event (Figure 4.9). In North Fork Bens Creek, calcium increased during the initiation of snowmelt and then decreased until the hydrograph peaked (Figure 4.10). ANC decreased during both of the snowmelt events in Biscuit Brook. ANC undoubtedly decreased during the snowmelt event at the North Fork Bens Creek but this is obscured due to the fact that ANC values

< 10 ueq/l were not analytically determined for this site (See Section 4.3).

4.4.2 Storm Episodes

Storm episodes occurred at all the study sites. The magnitude and duration of episodes, however, varied seasonally within sites and among sites. During the winter-spring period, when soils were generally saturated, runoff was significantly higher at all sites than during the summer-fall period (e.g., Figure 2.2). Peak discharge during this period was greater per unit of precipitation than during other periods (Table 4.11) except for the storm event resulting from Hurricane Gloria at Biscuit Brook (i.e. 26-28 September 1985). For example, 3.81 cm of rainfall in the East Fork Saline River watershed in December 1984, following the fall rainy season, resulted in a peak discharge of 1.8 m^3/s whereas 4.06 cm of rainfall in October 1985 following the dry low flow summer season resulted in a peak discharge of 0.13 m^3/s - or an order of magnitude lower flow. Large flows generally resulted in the greatest changes in stream chemistry but small increases in discharge under certain conditions had a significant effect on ANC. For example, the ANC depression associated with the 1.8 m^3/s East Fork Saline River discharge was about 50 ueq/l whereas the ANC depression associated with the 0.13 m^3/s discharge was over 76 ueq/l (Table 4.11). More importantly, the changes in hydrogen ion concentrations for these two events were only 0.47 (1.8 m^3/s) and 0.02 ueq/l (0.13 m^3/s).

The duration of storm episodes generally was shorter than snowmelt episodes. Storm episodes lasted from less than 24 hrs to about 48 hrs in the watersheds (Figures 4.11 - 4.16).

In the northeast watersheds pH values remained less than 5.5 for 10-25 hours during some storms (Figures 4.11 - 4.12). The minimum pH values recorded during storm episodes in northeastern sites generally were lower than in southeastern

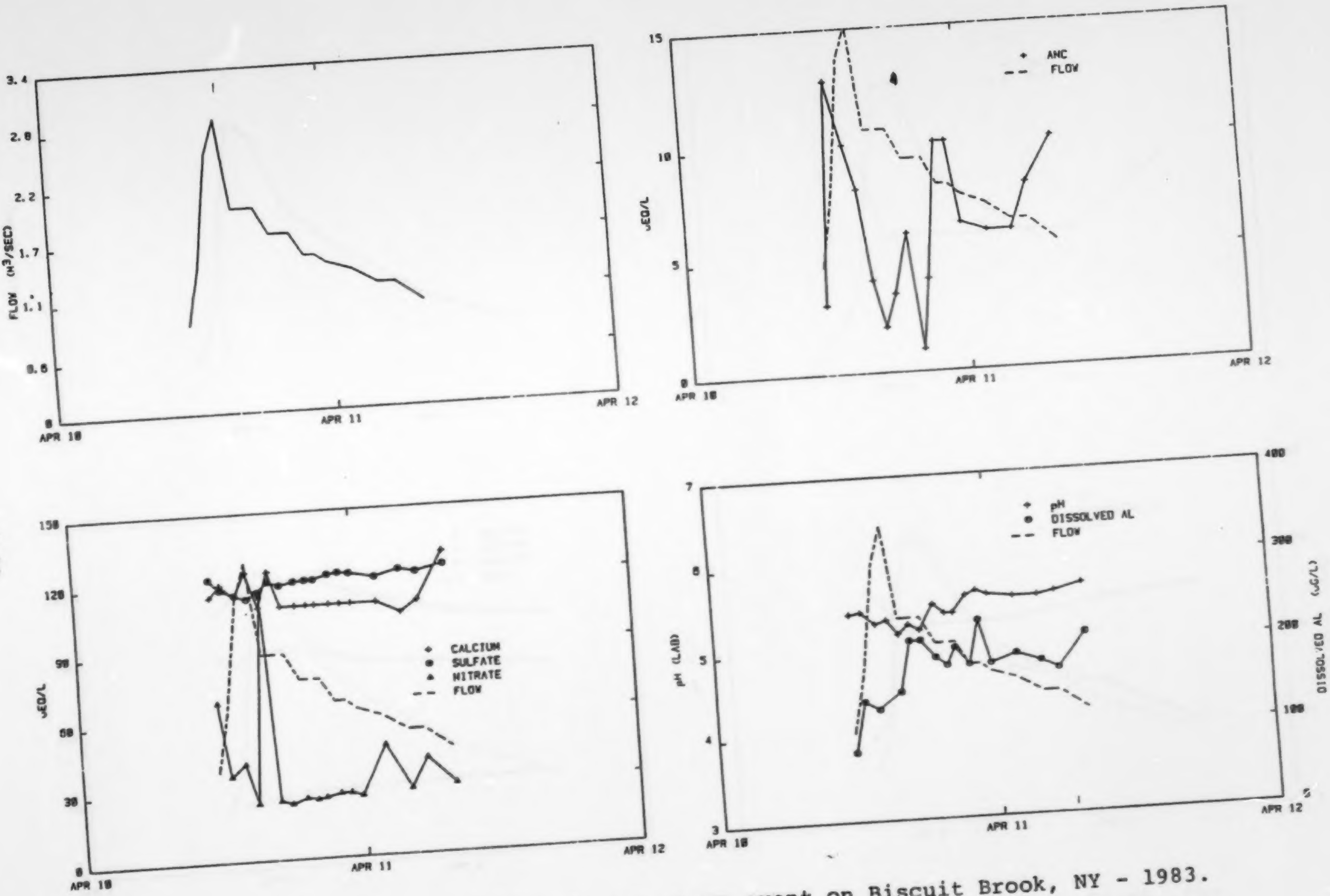

Figure 4.11. Selected variables from a storm event on Biscuit Brook, NY - 1983.

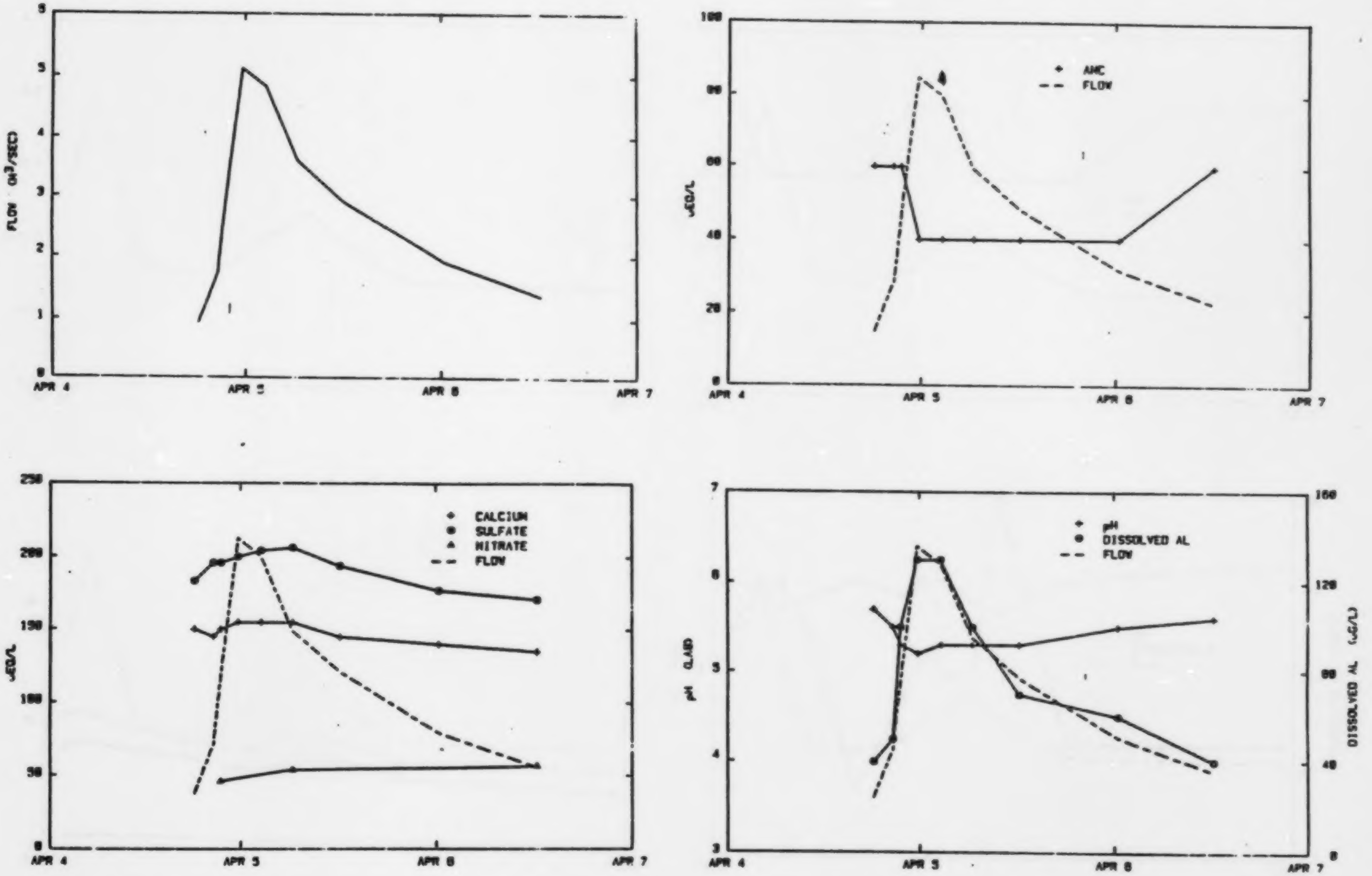

Figure 4.12. Selected variables from a storm event on South Fork Bens Creek, PA-1984.

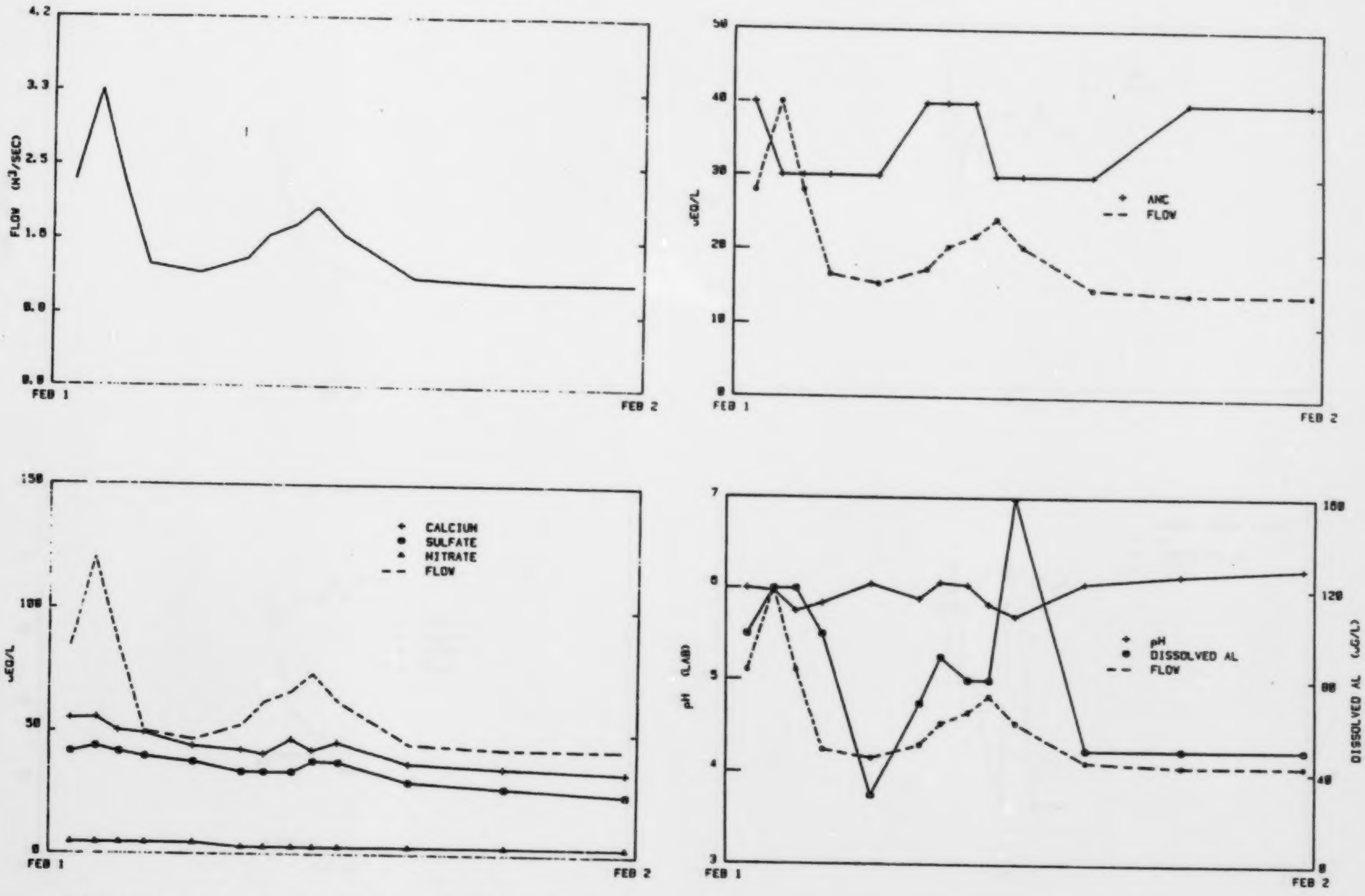

Figure 4.13. Selected variables from a storm event on Jarrett Creek, NC - 1985.

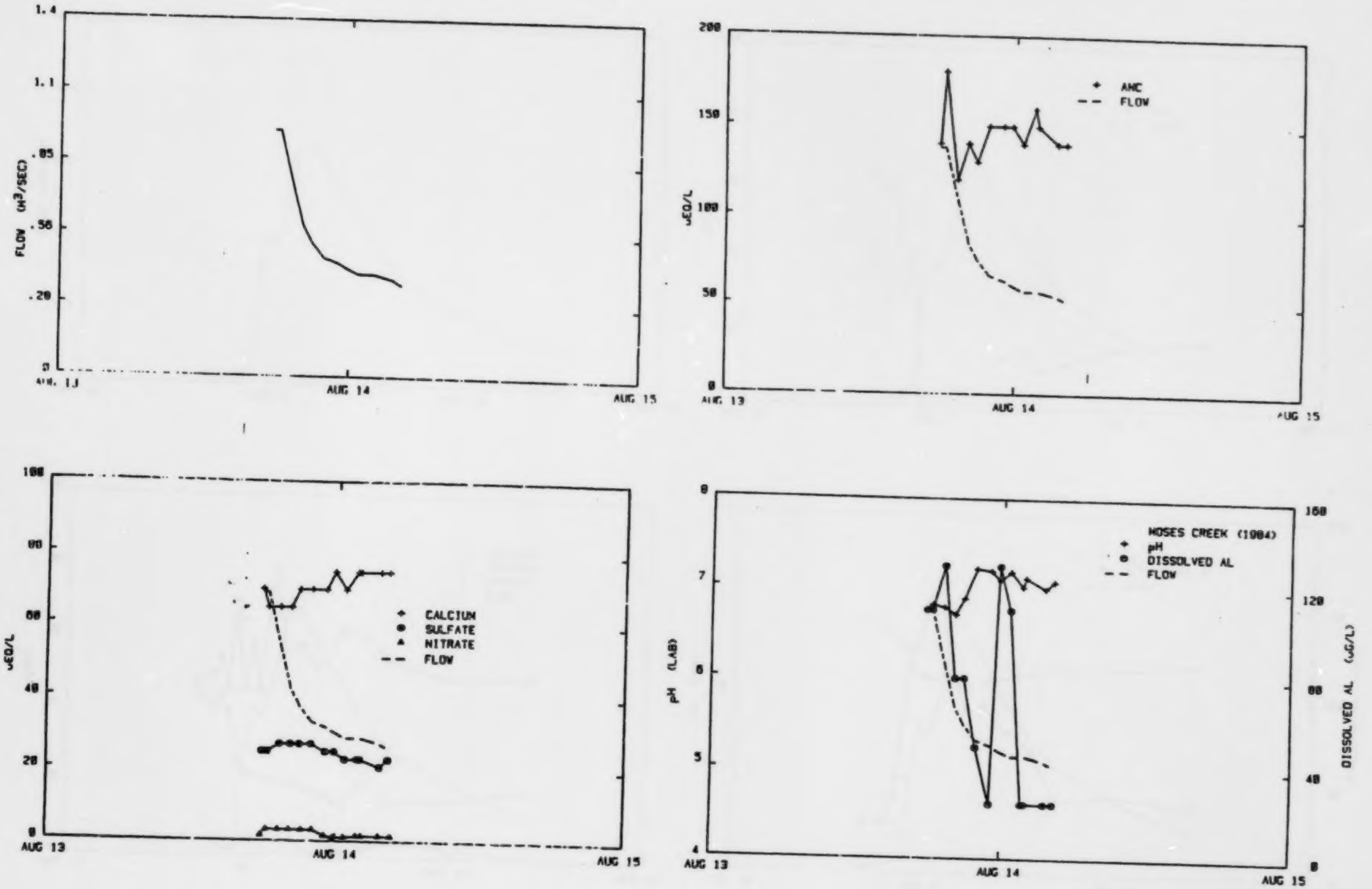

Figure 4.14. Selected variables from a storm event on Moses Creek, NC - 1984.

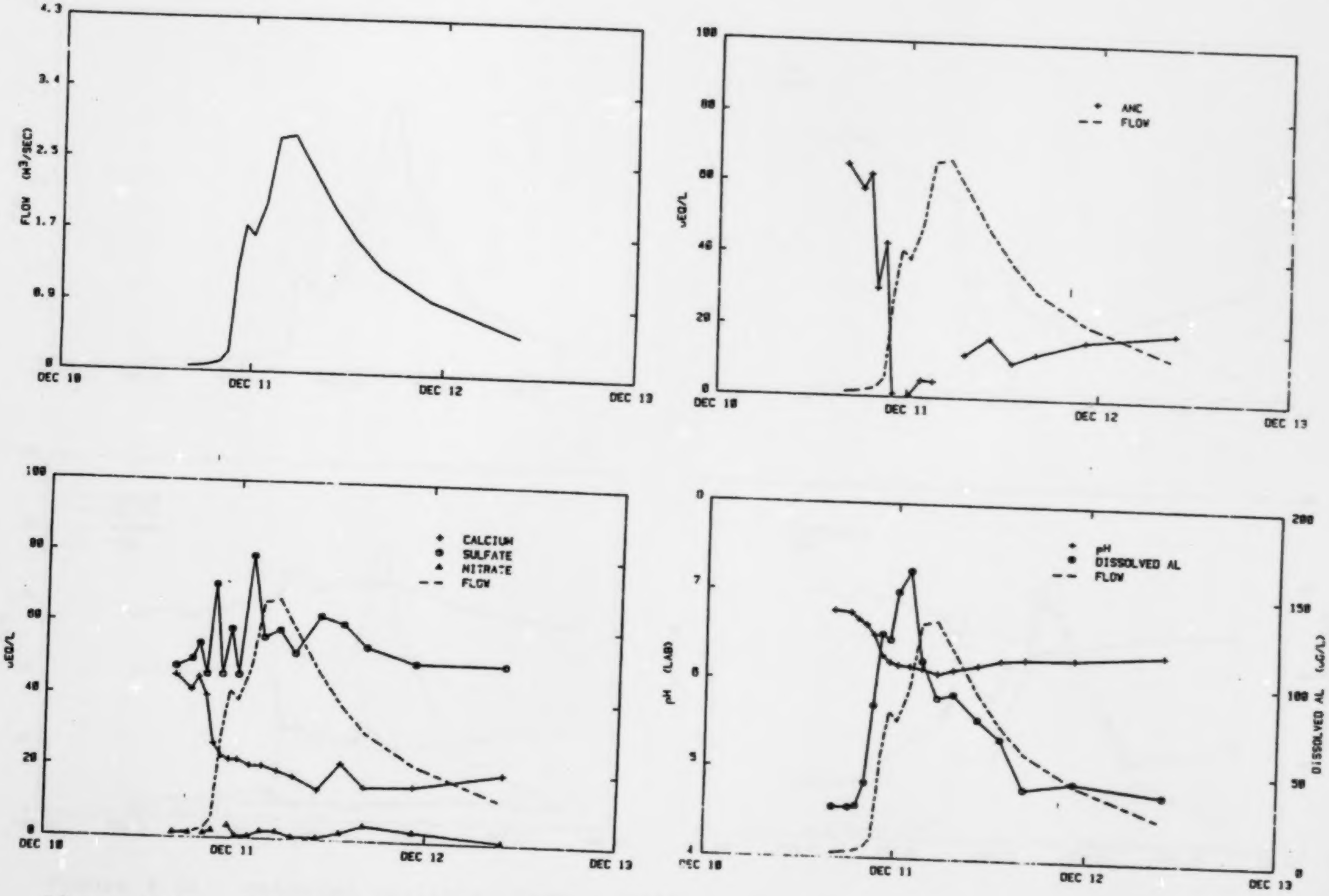

Figure 4.15. Selected variables from a storm event on East Fork Saline River, AR - 1984.

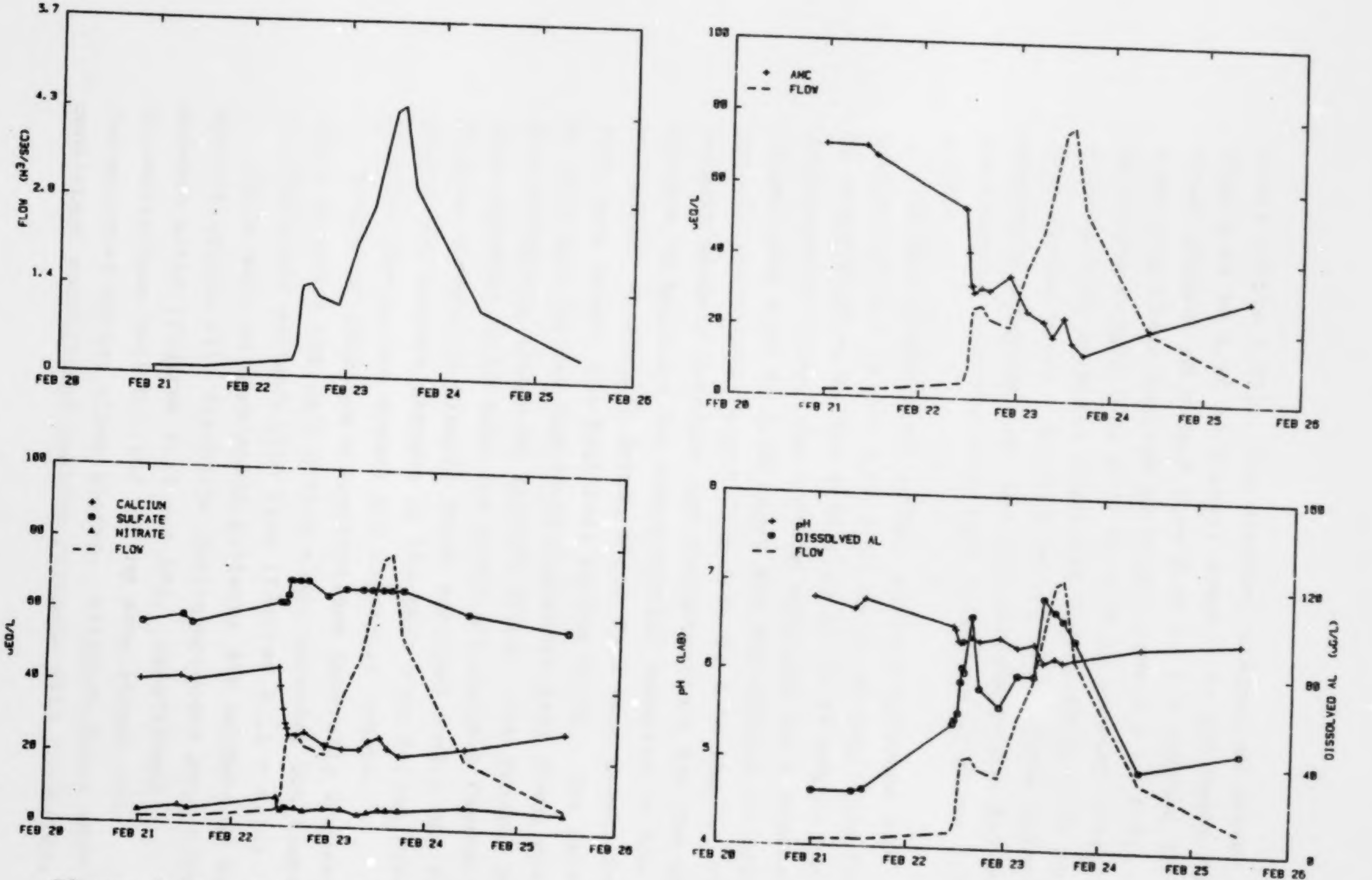

Figure 4.16. Selected variables from a storm event on East Fork Saline River, AR - 1985.

sites (Table 4.11). For example, minimum pH values ranged from 4.89 to 6.18 in Biscuit Brook. In the North Fork Bens Creek minimum pH ranged from 5.19 to 5.9 whereas in the South Fork Bens Creek minimum pH ranged from 5.1 to 6.21. Minimum pH values ranged from 5.70 to 6.07 in Jarrett Creek, from 6.07 to 6.99 in Moses Creek and from 6.08 to 7.09 in East Fork Saline River. Minimum pH values in storm episodes generally occurred near the peak discharge but did not necessarily coincide with peak discharge (Figures 4.11 - 4.16).

At the northeastern sites, maximum hydrogen ion concentrations ranged from 0.66 to 12.78 ueq/l and the change in concentration varied from 0.26 to 12.25 ueq/l. At the southeastern sites, the maximum hydrogen ion concentrations ranged from 0.08 to 1.98 ueq/l and the changes in hydrogen ion concentrations ranged from 0.01 to 1.14 ueq/l. The largest maximum hydrogen ion concentrations and the greatest changes in hydrogen ion concentration occurred in the winter and spring at Biscuit Brook, North Fork Bens Creek, South Fork Bens Creek, and East Fork Saline River. One exception to this pattern was the 26-28 September 1985 event resulting from Hurricane Gloria at Biscuit Brook. The general pattern also appeared to be true for Moses and Jarrett Creeks. Minimum changes in Biscuit Brook occurred during the November events and minimum changes in the East Fork Saline River occurred during the August and September events.

Dissolved aluminum concentrations generally increased and often exceeded 100 ug/l during storm episodes but there was no consistent pattern with flow (Figures 4.11 - 4.16).

There were no consistent patterns for sulfate or nitrate concentrations with discharge during episodes at a site or between sites (Figures 4.11 - 4.16). Constituent concentrations were diluted during some storms and concentrated during other storms. Although there were no consistent constituent loading patterns with discharge, increases or decreases in constituent concentrations during the event were noted and recorded in Table 4.12. As a result there were some general observations. For example, sulfate concentrations decreased during storm events in Biscuit Brook, NY, but increased or remained relatively constant during storms at all the other sites. Nitrate concentrations typically increased during storm flow at all sites except the North Fork Bens Creek site where it generally decreased or remained the same (Table 4.12).

Base cations and ANC generally were diluted during the storms at all sites (Figures 4.11 - 4.16) but remained relatively constant during some storms (Table 4.12).

4.4.3 Mean Event Chemistry

Mean event concentrations were calculated by summing the total accumulated mass during an event and dividing by the total water load or discharge during the same interval. These concentrations are compared with mean annual flow-weighted concentrations in Table 4.13. The mean storm composition is illustrated in Figure 4.17.

4.4.3.1 pH - pH values were lower during events at all sites (Table 4.13). The greatest pH difference between mean event and flow-weighted baseflow values was 0.9 in Biscuit Brook. At North Fork Bens Creek and Moses Creek the difference was only 0.1, but at South Fork Bens Creek it was 0.5, at Jarrett Creek it was 0.6, and at the East Fork Saline River it was 0.4.

The difference of 0.9 pH units at Biscuit Brook represented on increase in mean event hydrogen ion concentration of 6.9 ueq/l over mean annual baseflow concentration (Table 4.13). North and South Fork Bens Creeks mean event hydrogen ion concentrations increased 1.1 and 1.4 ueq/l, respectively, over base flow concentrations. The largest increases in mean event hydrogen ion concentrations occurred at these northeastern sites. At the southeastern

Table 4.12. Relative change in concentration of stream constituents during episodes.

BISCUIT BROOK

Dates	Precip (cm)	Flow Range (m^3/s)	Change		
			Base Cation	SO_4	NO_3
Apr 10-11, 1983	-	0.57-2.92	-	-	+
Nov 10-11, 1983	4.06	0.03-0.19	-	-	+
Mar 21, 1984	4.83*	0.37-0.79	-	-	+
Apr 3-6, 1984	5.95*	0.37-18.58	-	-	+
Nov 5, 1984	2.21	0.03-0.17	-	-	+
Feb 23-26, 1985	3.56*	0.13-2.32	Ca+, Na-	-	+
Mar 11-13, 1985	0.38*	0.18-2.38	Ca+, Na-	-	+
Jul 31, 1985	1.83	0.19-1.08	Ca-, Na**	-	*
Sep 26-28, 1985	17.37	0.08-21.14	***	-	+

NORTH FORK BENS CREEK

Dates	Precip (cm)	Flow Range (m^3/s)	Change		
			Base Cation	SO_4	NO_3
Dec 19-21, 1984	4.22	0.31-0.65	**	**	**
Feb 22-28, 1985	*	0.12-1.13	-	+	+
Mar 12-13, 1985	2.77	0.28-0.51	Ca+, Na-	+	**
May 2-4, 1985	5.84	0.11-1.47	-	+	-
Jul 8, 1985	0.18	0.10-0.45	-	**	-

SOUTH FORK BENS CREEK

Dates	Precip (cm)	Flow Range (m^3/s)	Change		
			Base Cation	SO_4	NO_3
Apr 4-6, 1984	6.10	0.91-3.57	+	+	+
Aug 13-15, 1984	6.15	0.65-1.67	+	+	+

JARRETT CREEK

Dates	Precip (cm)	Flow Range (m^3/s)	Change		
			Base Cation	SO_4	NO_3
Nov 28-29, 1984	3.84	0.33-4.77	-	+	+

Table 4.12. Continued.

MOSES CREEK

Dates	Precip (cm)	Flow Range (m^3/s)	Change Base Cation	Change SO_4	Change NO_3
Aug 13-14, 1984	1.91	0.37-0.98	-	+	+
Nov 28, 1984	0.89	0.31-1.32	-	+	+
Apr 5-6, 1985	2.24	0.24-0.95	-	+	-

EAST FORK SALINE RIVER

Dates	Precip (cm)	Flow Range (m^3/s)	Change Base Cation	Change SO_4	Change NO_3
Dec 13-17, 1984	3.81	0.14-1.76	-	+	+
Feb 20-25, 1985	9.14	0.11-4.35	-	+	+
Mar 19-22, 1985	6.35	0.09-2.22	-	+	+
Aug 5, 1985	1.27	0.03-0.05	**	-	+
Sep 13-14, 1985	2.79	0.04-0.05	-	+	+
Oct 18-20, 1985	4.06	0.11-0.13	-	**	**
Dec 10-12, 1985	6.60	0.06-2.85	-	+	+

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* = Snowmelt event or combination rainfall/snowmelt event

- = Decrease

+ = Increase

** = No Change

*** = Insufficient Data

Table 4.13. Comparison of mean event and mean annual baseflow concentrations (all units are ueq/l except pH which is s.u. and aluminum which is ug/l).

	Cations						
Study Sites	pH	H	Ca	Mg	Na	K	Al
Biscuit Brook	5.1	7.9	99.6	34.5	15.5	8.4	205.0
	(6.0)*	(1.0)	(123.7)	(45.1)	(17.5)	(5.5)	(69.3)
North Fork Bens Creek	5.3	5.0	165.2	79.0	46.1	16.9	130.4
	(5.4)	(3.9)	(160.0)	(76.8)	(61.3)	(15.7)	(101.6)
South Fork Bens Creek	5.7	2.0	151.2	75.7	17.8	16.9	63.0
	(6.2)	(0.6)	(167.5)	(84.4)	(23.1)	(18.7)	(48.6)
Jarrett Creek	6.2	0.6	40.5	37.0	50.0	7.4	141.2
	(6.8)	(0.2)	(42.9)	(34.9)	(50.6)	(10.9)	(30.6)
Moses Creek	7.0	0.1	63.9	43.6	49.6	24.8	98.9
	(7.1)	(0.1)	(63.7)	(40.4)	(54.1)	(14.6)	(36.9)
East Fork Saline River	6.2	0.6	20.7	41.2	38.2	13.0	76.4
	(6.6)	(0.2)	(33.6)	(43.3)	(44.1)	(12.4)	(27.0)

	Anions			
Study Sites	ANC	SO_4	NO_3	Cl
Biscuit Brook	-3.0	107.9	34.6	11.3
	(15.5)	(138.4)	(20.2)	(17.7)
North Fork Bens Creek	16.8	208.7	12.3	56.4
	(43.1)	(206.3)	(46.4)	(83.4)
South Fork Bens Creek	11.0	186.6	11.8	22.3
	(78.6)	(190.3)	(52.2)	(27.2)
Jarrett Creek	36.9	38.9	2.6	58.7
	(68.0)	(18.2)	(1.3)	(32.3)
Moses Creek	125.3	28.7	1.8	20.6
	(135.9)	(22.0)	(1.0)	(15.3)
East Fork Saline River	23.1	61.2	0.6	30.7
	(58.8)	(54.1)	(2.4)	(36.4)

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* Mean annual concentration in parentheses.

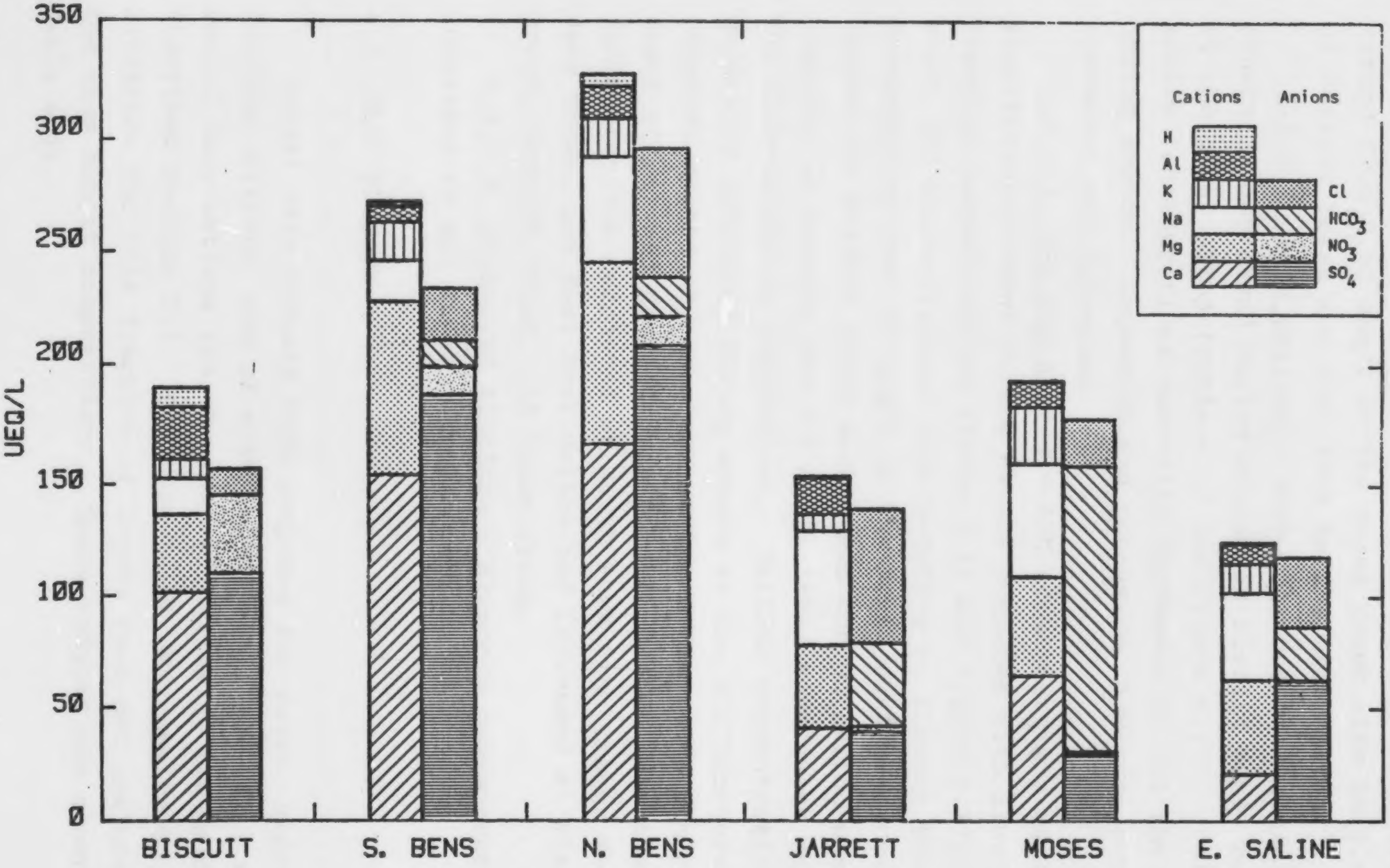

Figure 4.17. Mean event stream chemistry concentrations.

sites, the increases in mean event hydrogen ion concentrations over mean annual base flow concentrations ranged from 0.02 ueq/l at the Moses Creek site to 0.4 ueq/l at Jarrett Creek and East Fork Saline River sites.

4.4.3.2 Base Cations - Base cation concentrations generally decreased during storms in Biscuit Brook but varied at the other sites (Table 4.13 and Figure 4.17). Calcium and sodium concentrations generally decreased at all the sites during events. Magnesium and potassium, however, both increased and decreased.

4.4.3.3 ANC and Anions - ANC concentrations were significantly lower during events compared with flow-weighted baseflow concentrations (Table 4.13 and Figure 4.17). Mean event ANC concentrations were negative at Biscuit Brook and decreased by over 60 ueq/l in the South Fork Bens Creek. The reason the Biscuit Brook mean event concentration was negative is because the 3-6 April 1984 storm event dominated the flow-weighting computation. Sulfate concentrations generally increased during events at the southeastern sites, remained relatively constant at the North and South Fork Bens Creek sites, and decreased in Biscuit Brook. Nitrate concentrations decreased at North Fork Bens Creek, South Fork Bens Creek, and East Fork Saline and increased at Biscuit Brook, Jarrett Creek, and Moses Creek.

4.4.3.4 Dissolved Aluminum - Aluminum concentrations increased at all sites during events.

4.5 MASS BUDGETS

Annual mass budgets were computed for water, hydrogen, sulfate, nitrate, sum of acid anions (SO_4, NO_3, Cl), and the sum of base cations (Ca, Mg, Na, K) following the method described Section 3.5. Dry deposition was considered, but estimates for this fraction of inputs were not included in the mass budget computations. These budgets are shown in Table 4.14.

Table 4.14. Annual mass budgets.

	Input	Output	I-O	Percent Retention
Biscuit Brook (Oct 83 - Sep 84)				
Water, cm	168.0	110.8	57.2	34
H^+, eq/ha	477	12	465	97
SO_4, eq/ha	463	1596	-1131	-244
NO_3, eq/ha	255	228	27	11
Sum Anions, eq/ha	803	2234	-1431	-178
Sum Base Cations, eq/ha	182	2275	-2093	-1150
South Fork Bens Creek (Oct 83 - Sep 84)				
Water, cm	148.8	92.2	56.6	38
H^+, eq/ha	1207	10	1197	99
SO_4, eq/ha	1248	1756	-508	-41
NO_3, eq/ha	599	517	82	14
Sum Anions, eq/ha	1958	3769	-1811	-92
Sum Base Cations, eq/ha	425	2723	-2298	-541
Jarrett (May 84 - Mar 85)[1]				
Water, cm	159.0	124	35	22
H^+, eq/ha	454	2	452	100
SO_4, eq/ha	495	220	275	56
NO_3, eq/ha	230	15	215	93
Sum Anions, eq/ha	808	1495	-651	-81
Sum Base Cations, eq/ha	188	1700	-1512	-804

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[1] Period prorated by a factor of 12/11 to obtain annual budgets.

Table 4.14. Annual mass budgets (Con't).

	Input	Output	I-O	Percent Retention
Moses (May 84 - Mar 85)[1]				
Water, cm	127.0	110	17	13
H^+, eq/ha	397	1	396	100
SO_4, eq/ha	436	238	198	45
NO_3, eq/ha	197	12	185	94
Sum Anions, eq/ha	840	1833	-993	-118
Sum Base Cations, eq/ha	161	1857	-1696	-1053
East Fork Saline (Nov 84 - Oct 85)				
Water, cm	152.0	80.6	71.4	47
H^+, eq/ha	401	2	399	100
SO_4, eq/ha	537	491	46	9
NO_3, eq/ha	279	21	258	92
Sum Anions, eq/ha	1013	1386	-373	-37
Sum Base Cations, eq/ha	453	1285	-832	-184

4.5.1 Water Budget

Water budgets were calculated for each site and were discussed, in part, in Section 4.1., Water Budget. The difference between water input and water output represents the change in storage in the watershed and losses due to evapotranspiration (ET). Murdoch (1986) indicated ET dominated this difference in the Catskills. Water losses were similar at Biscuit Brook and South Fork Bens Creek, lowest in the SBRP sites, and highest in the East Fork Saline.

4.5.2 Hydrogen

The hydrogen ion budgets for all sites indicated significant hydrogen ion retention in the watersheds or significant increases in pH from the incoming precipitation to the stream water (Table 4.14).

4.5.3 Sulfate

The northeastern sites (i.e., Biscuit Brook and South Fork Bens Creek) both had a net export of sulfate from the watersheds (Table 4.14) whereas the southeastern sites (i.e. Moses Creek, Jarrett Creek and East Fork Saline) were retaining sulfate.

4.5.4 Nitrate

The Biscuit Brook and South Fork Bens Creek watersheds were near nitrate steady-state (Table 4.14). The other watersheds had significant retention of nitrate.

5.0 DISCUSSION

Stream chemistry represents the integrated response of watershed and stream processes to acidic inputs. This response is a function of many factors such as deposition chemistry, interactions with the forest canopy, the flow path of water through the watershed and its interaction with exchange sites and complex reactions occurring in the soil, site geology and mineral weathering, biotic processes such as uptake, transformation and translocation both in the watershed and the stream. A State of Science review of Acidic Episodes in Surface Waters has been prepared by Marmorek et al. (1986) that can be referenced for a general discussion of factors and processes important in acidic episodes.

This section focuses on factors that may influence the identification and interpretation of regional patterns based on results from the four study sites. Regional patterns, inferred from these data, should be considered to be speculative because four sites are insufficient to provide reasonable estimates of patterns within a region, let alone among regions. Although a total of over 30 storms were sampled, this represents an average of less than eight storms per region and less than two storms per season. In addition, few large storms were sampled in these studies, although this may be representative of the occurrence of large storms.

Episodes are, by definition, a subset of hydrometeorological events based on acidification occurring during the event. To understand episodic responses and effects requires an understanding of the hydrologic response of the system and how various watershed processes modify meteorological inputs to produce the integrated stream response. The following sections will discuss these interactions and focus on:

- Study site;
- Deposition chemistry;
- Watershed response;
- Stream response;
- Watershed budgets;
- Frequency of episodes;
- Discharge-concentration relations; and
- Limitations of these analyses.

5.1 STUDY SITES

As stated above, an attempt to infer regional patterns from these four study sites will be made. Before such an attempt can be made, two questions must be addressed:

- Are the sites similar to each other?; and
- Are the sites typical of the region?

As was shown in Section 2.1 and Table 2.1, the sites are similar to each other based upon physiographic characteristics such as drainage area, stream width, depth, and stream gradient. All the sites also are located in mountainous terrain with predominantly deciduous forest cover. Furthermore, the sites had continuous flows and supported fish (e.g., trout or smallmouth bass). Because the sites do differ in terms of geology and soils, these factors must be considered when making comparisons between sites and regions.

The second question is the more difficult to address. Originally, the principal investigators (Murdoch, Nix and Thornton, Olem, Witt and Barker) selected the sites so the watersheds would be typical or at least not atypical of other watersheds in the regions (i.e., the Catskill Mountains, NY, Laurel Hill, PA; the Southern Blue Ridge Province, TN and NC; and the Ouachita Mountains, AR). This selection was based on physiographic characteristics and the local expertise of the principal investigators. Field reconnaissance of the study sites verified that the study streams visually appeared to be similar to others in the regions based on physiographic characteristics, soil type, geology, and forest cover.

All of the sites received acidic deposition during the study period. Comparisons of wet deposition quantity and quality identified differences between the study sites and NADP/NTN monitoring stations located within a 400 km radius of the study sites (Section 4.2 and Table 4.1) but these differences should be expected because of the large spatial and temporal variability in rainfall.

For the above reasons, the study sites should be considered reasonably typical of the regions in which they are located.

5.2 DEPOSITION CHEMISTRY

Wet deposition chemistry measured at each site generally reflected the regional patterns observed from NADP/NTN data and described by the NAS (1986) for the Eastern United States. Each of the study sites, however, was located in mountainous terrain, so differences between site specific observations and regional values should be expected. Temporal and spatial variability in precipitation in mountainous regions is well-recognized. This variability can influence watershed response to acidic deposition. For example, if the rate of acidic input is high, it may exceed the assimilative or acid neutralization capacity of the watershed during snowmelt or storm events.

Seasonal variability in deposition quantity and quality was measured at each site. Rainfall was generally low during the fall and high during the spring. There was no general relation between maximum pH and rainfall. Precipitation pH, however, was inversely related with sulfate concentrations on both a seasonal and annual basis.

No other patterns in precipitation chemistry were apparent (Table 4.2). This, in part, might be because the NADP/NTN seasons (Section 3.1) are not representative of hydrometeorological seasons in the different regions of the United States. For example, the summer season (June-August) is a transition season from wet to dry periods in all regions but the SBRP (Figure 2.2). A July-September season would be more representative of dry, low flow conditions. Selection of hydrometeorological seasons might have resulted in the identification of underlying seasonal patterns.

The comparison of rainfall acid anions indicated the Northeast had higher sulfate and nitrate concentrations than the Southeast, although the East Fork Saline River, AR site had acid anion concentrations (e.g., SO_4, NO_3, Cl) comparable to Biscuit Brook, NY. Rainfall at the East Fork Saline site also had lower pH and higher sulfate values than the Coweeta site although the average regional rainfall chemistry for these two regions was consistent with previously published results (e.g., Figure 2.5 and 2.6). There also were regional differences in total precipitation and precipitation intensity. The SBRP and Ouachita Mountains have an average of 50-70 days of thunderstorm activity per year compared with 30-50 days in Laurel Hills and 10-30 days in the Catskills (Figure 5.1). It is apparent that the probability an event will occur is different between the regions.

There was considerable variability among events both within seasons and among seasons at the study sites. Jeffries et al. (1979) studied 39 events in central Ontario and found loading per event varied over an order of magnitude for most major ions and over two orders of magnitude for hydrogen ions. An important consequence of large inter-event variability is that relatively few events can contribute a large fraction of the total deposition over a given period (Harvey et al. 1981). A frequency

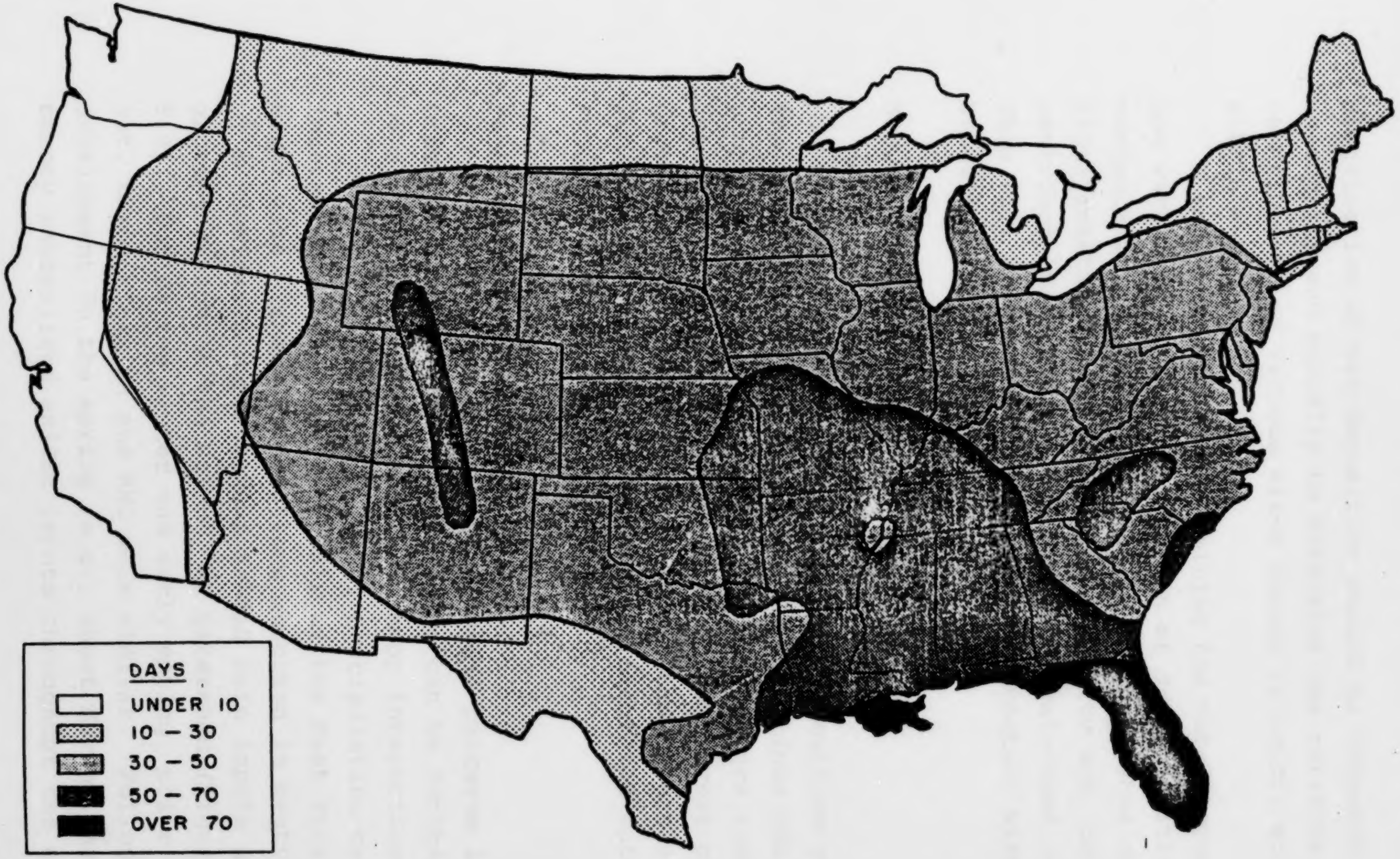
DAYS
UNDER 10
10 — 30
30 — 50
50 — 70
OVER 70

Figure 5.1. Average number of days of thunderstorm per year (after Geraghty et al. 1973).

distribution of wet deposition should be computed both seasonally and annually to determine the relative contribution of various sized storms to acidic episodes within a region.

A major unknown in determining the total deposition to the watershed is the contribution of dry deposition. The accumulation of dry deposition in the watershed can significantly increase the runoff acidity and, obviously, contribute to the total acid load the watershed receives. This will be discussed further in conjunction with the mass budgets.

5.3 WATERSHED RESPONSE

The watershed response to acidic deposition represents the integration of acidic inputs with various watershed components. These components include factors such as interception of acidic deposition by the forest canopy, processes occurring within the soils and watershed geology. The stream chemistry reflects this integrated watershed response to atmospheric deposition.

5.3.1 Canopy Interactions

The consequent effects of seasonal patterns in precipitation chemistry noted above can be further modified by watershed processes such as canopy interactions.

Throughfall chemistry (i.e., precipitation-canopy interactions) was monitored only at the East Fork Saline River site. These interactions resulted in neutralization of a considerable portion of acidic rain inputs during the growing season in the Saline, AR watershed (Figures 5.2 - 5.3). During the winter and early spring, prior to leaf-out, throughfall pH and ANC were similar. Following canopy development in the spring (e.g., about March), however, the canopy neutralized acidic inputs throughout the summer and

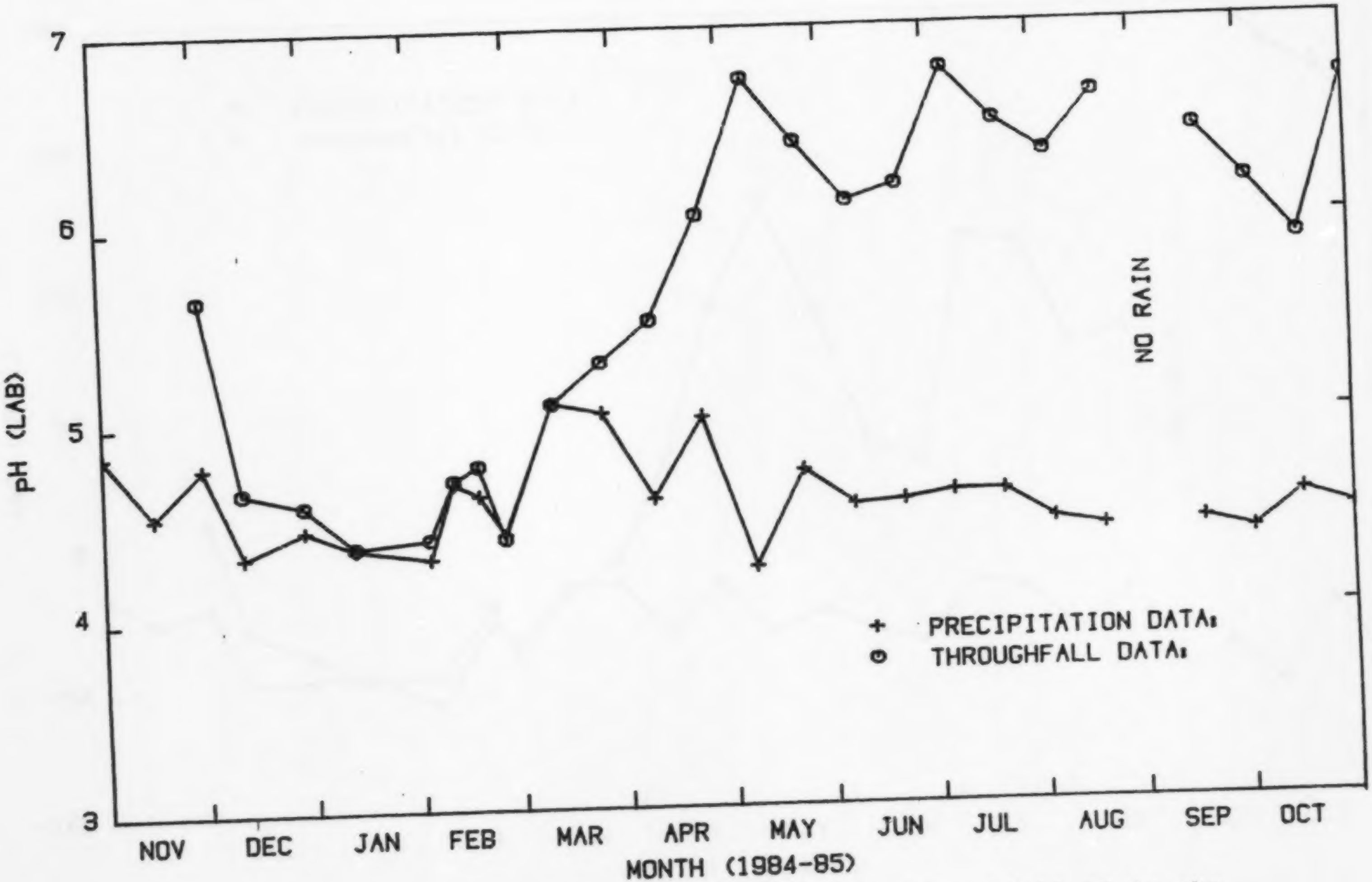

Figure 5.2. Comparison of precipitation and throughfall pH in the East Fork Saline River, AR.

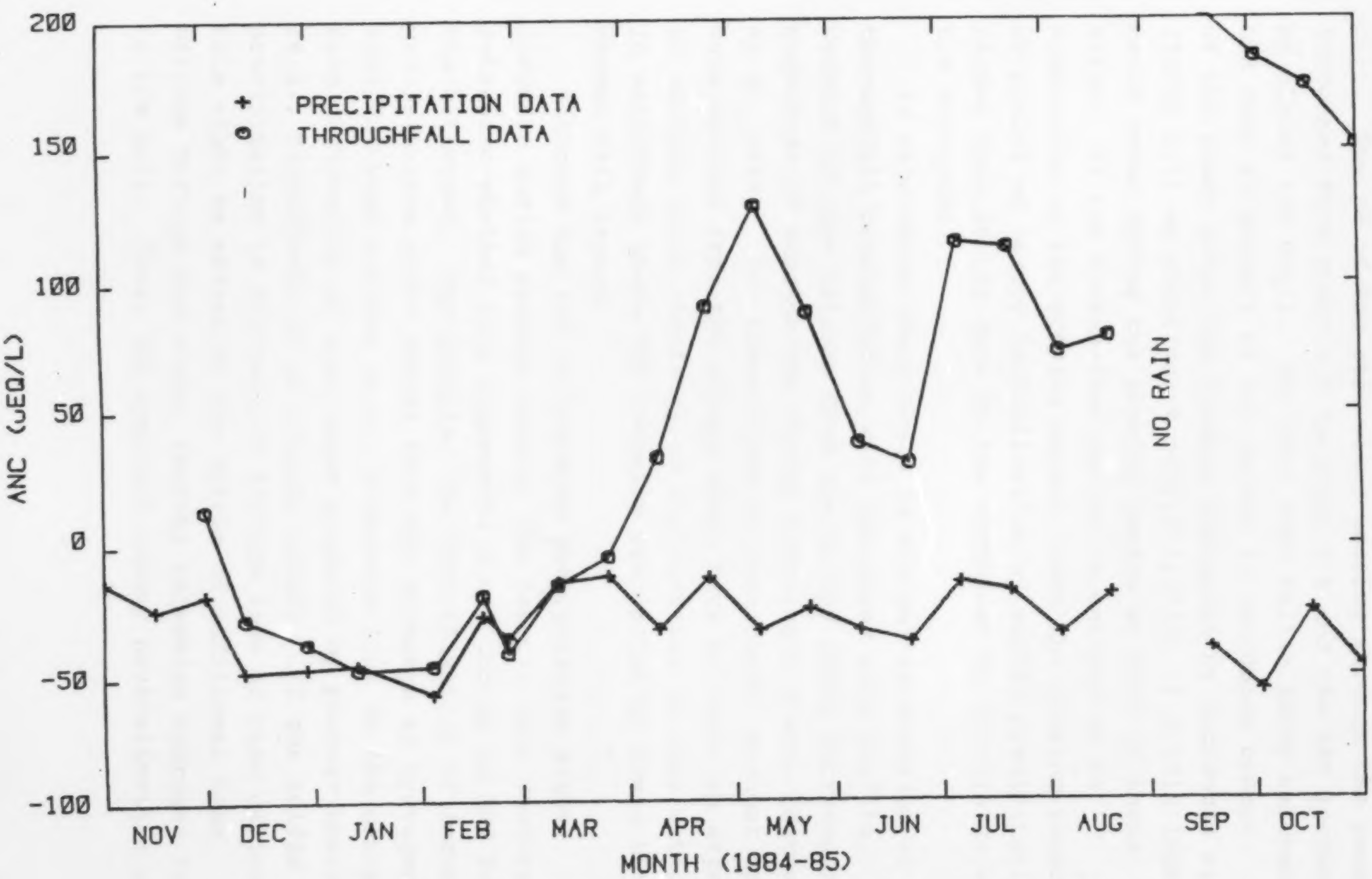

Figure 5.3. Comparison of precipitation and throughfall ANC in the East Fork Saline River, AR.

fall. The pH of the rain water passing through the canopy increased from about 4.5 to about 6.5 and the ANC increased by almost 100 ueq/l. The East Fork Saline River watershed had over 80 percent of the forest in deciduous canopy. All of the study sites had forests dominated by deciduous canopy (Table 2.1) so significant neutralization of acidic inputs could occur during the growing season at each of these sites. If the freeze-free period is assumed to be comparable to the growing season, then the growing season, or period of canopy neutralization of acidic precipitation, ranges from 90-180 days in the Northeast to 150-210 days in the Southeast.

In watersheds where there is minimal interaction of the throughfall precipitation with the upper soil profile, washout of base cations from the canopy could decrease the magnitude of depressions during hydrologic events (Marmorek et al. 1986). For these types of watersheds, washout of base cations from the canopy might have as large an effect on surface water chemistry as the increase in base cations in watersheds where the incoming precipitation moves through deeper soil layers.

Although the ANC of incoming precipitation might increase during passage through the canopy, many factors determine whether this represents a net change in ANC for the watershed. For example, the neutralization of incoming precipitation might result from the exchange of hydrogen ions for base cations (e.g., potassium ion) in the canopy or from protonation of weak bases produced by photosynthesis (e.g., bicarbonate or an organic anion). If the acidic precipitation is neutralized through loss of base cations, this might be offset by the uptake of additional base cations through the roots, thereby releasing hydrogen ions to the soil. Thus, the apparent canopy neutralization might or might not result in less net watershed acidification (Marmorek et al. 1986).

5.3.2 Geology

The dominant cation in Biscuit Brook, North and South Fork Bens Creek, and Moses Creek was calcium whereas sodium was the dominant cation in the East Fork Saline River and Jarrett Creek (Table 4.3 and Figure 4.3). The dominant geologic formation in the two northeastern watersheds was sandstone containing weathered feldspars. Calcium is a weathering product from feldspar (Drever 1982). Shale with some biotite was the dominant geological lithology in the southeastern watershed study sites. Weathering products from biotite and shale are magnesium and sodium (Drever 1982). Although Moses Creek was dominated by calcium rather than sodium, the two base cations had similar concentrations as opposed to the large differences between sodium and calcium at Biscuit Brook and South Fork Bens Creek.

Although interactions with soil are generally considered to be the most important processes influencing surface water acidification, the soil composition generally reflects the underlying geologic formation and parent material.

5.3.3 Soil Interaction

Soil processes such as base cation exchange and resupply and sulfate sorption are important in neutralizing acidic inputs (Church and Turner 1986). The interaction of acidic precipitation with these soil sites, however, is influenced by whether the incoming water reaches these exchange sites. There was virtually no overlap between the seasons of maximum/minimum precipitation chemistry (Table 4.2) and seasons of maximum/minimum stream chemistry (Table 4.4). This emphasizes the importance of watershed processes on stream chemistry.

The concentration of base cations and other constituents in surface waters depends on the flow path of water through the watershed (Johnson 1979, Jeffries and Semkin 1983, Schnoor et al. 1983, Chen et al. 1983, Driscoll et al. 1986). Minimum stream pH values and ANC concentrations occurred during the winter and spring periods at the study sites. These periods corresponded with snowmelt, when the ground was frozen, or storm events when the soil was saturated. During snowmelt or storm events, restricted percolation through saturated soils can minimize water contact with the lower mineral soils, and the neutralization of acidic inputs.

During snowmelt, base cation concentration can be reduced by dilution (Johnson et al. 1969). Dilution of base cations during episodes has been reported for systems in Maine (Haines and Akielaszek 1984), New York (Driscoll et al. 1986), Ontario (Harvey and Whelpdale 1985, Dillon and LaZerte 1985), Norway (Sullivan et al. 1986), France (Fritz et al. 1984), and Minnesota (Schnoor et al. 1984). Base cation concentrations, however, do not always decrease during snowmelt periods. Webb (1982) reported increased base cation concentrations during springmelt in a Norwegian river. Murdoch (1986) and Witt and Barker (1986) reported that in Biscuit Brook and North Fork Bens Creek, respectively, base cation concentrations increased at the initiation of snowmelt before decreasing during the remainder of the event. These authors attributed this initial increase to the water stored in the unconsolidated zone during gradual ice and snowmelt that had sufficient time to interact with the soil matrix. Runoff coefficients (i.e., discharge volume/precipitation volume) during this period were high at all sites, exceeding 1.0 in the northeastern study sites.

During the low flow summer and fall periods, pH, ANC, base cations, and sulfate were near maximum concentrations at all study sites except Jarrett Creek. Several factors contributed to these higher constituent concentrations. First, the majority of the flow during these periods was contributed by subsurface or groundwater flow. Second, evapotranspiration was high during the growing season, soil moisture was lower and constituents were concentrated in the soil solution. There was little runoff during this period so soil contact time with incoming precipitation was likely to be long. Third, soil pCO_2 was higher because of temperatures and plant growth resulting in higher weak acid weathering. Fourth, throughfall had higher base cation and ANC concentrations because of canopy interactions with precipitation.

Biotic interactions also influenced nitrate concentrations. At all sites, minimum nitrate concentrations corresponded with the summer-fall period (i.e., the active vegetative growing season). Maximum nitrate concentrations corresponded with the winter-early spring season (i.e., the period during which the vegetation was dormant). Nitrate mobility should be greatest during the winter season and potentially contribute to the generation of acidic episodes during this period. This was indicated by the nitrate pulse during snowmelt at Biscuit Brook.

A major difference between northeastern streams and southeastern streams was the sulfate concentration, which was greater in the northeastern streams (i.e., Biscuit Brook and North and South Fork Bens Creek). If sulfate moves as a mobile anion, cations must also be transported to maintain electroneutrality (Galloway et al. 1984). Sulfate adsorption by watershed soils can reduce sulfate mobilization and, therefore, reduce both cation and anion concentrations in the stream water. Soils at the northeastern sites are predominantly Inceptisols and Spodosols. Soils at the southeastern sites are Ultisols. Johnson (1984) indicated Ultisols generally have greater sulfate sorptive capacity than Inceptisols and Spodosols. This might account for some of the differences between the northeastern and southeastern sites. There are indications, however, that the East Fork Saline River sites might be approaching sulfate steady state. Although the soils are Ultisols, the watershed soils are extremely thin.

5.4 STREAM RESPONSE

Although flows were generally high in the spring and low in the fall at all study sites, the stream responses to hydrometeorological inputs were highly regionalized. In the northeastern sites, snowmelt (often triggered by, or associated with, rainfall) was the dominant event. Snowmelt can occur at almost anytime during the winter and spring. For example, the February 22-28, 1985 event at the North Fork Bens Creek was a snowmelt event. This event was of longer duration (i.e., 160 hours) than the rainstorm events and resulted in a pH decline of 0.8 units (i.e., ΔH^+ of 4.96 ueq/l). The stream pH during the event was less than 5.5 for about 130 hr. This contrasts to rainfall events at the northeastern sites that ranged in duration from 36 to 48 hrs with pH values less than 5.5 for 10-25 hr.

As noted above, a confounding factor is when rainfall and snowmelt occur concurrently. For example, on February 23-26, 1985 and April 4-6, 1984 at Biscuit Brook and South Fork Bens Creek, respectively, rainfall and snowmelt occurred concurrently resulting in some of the highest peak flow values at Biscuit Brook and South Fork Bens Creek. The pH minimum at South Fork Bens Creek was among the lowest minimum pH values (i.e. 5.2) recorded at this site and the change in pH was one of the largest changes observed at the site (i.e., 0.7 pH units or ΔH^+ of 5.05 ueq/l). At Biscuit Brook, the pH change during the February 23-26, 1985 event was 1.0 but, because of the higher initial pH, the change in H^+ was 3.55 ueq/l. The April 3-6, 1984 and the September 26-28, 1985 events at Biscuit Brook resulted in a greater pH change. The September event was associated with Hurricane Gloria. The high peak flow during the April 3-6, 1984 event was probably influenced by high antecedent moisture conditions from the March 21, 1984 event and snowmelt occurring in the higher elevations (Murdoch, personal communication).

There was considerable variability among events both within seasons and among seasons at the study sites. For example, at Biscuit Brook during the spring season (March, April and May), precipitation on March 21, 1984 was 4.83 cm, which produced a peak flow of 0.79 m^3/s, a pH change of 0.32 and an ANC concentration change of 4.0 ueq/l. Thirteen days later another event occurred. The precipitation was 5.95 cm (i.e., 1.12 cm more rain), which produced a peak flow of 18.58 m^3/s, a 1.28 pH unit change and 32.0 ueq/l ANC concentration change. Antecedent soil moisture conditions can have a significant influence on runoff and subsequent stream chemistry. During the winter (defined as November, December, and January) at the southeastern East Fork Saline River site, rainfall varied from 4-9 cm the changes in stream pH and the minimum pH depressions ranged from 0.51 to 0.70 pH units (i.e., ΔH^+ from 0.67 to 0.47)and from 6.08 to 6.17, respectively. In the fall (September, October, and November), the rainfall varied from 3-4 cm and change in stream pH ranged from 0.14 to 0.26 with the minimum pH depression ranging from 6.66 to 7.09.

Increases in sulfate, nitrate, and/or organic acids have been associated with pH depressions during acidic episodes (Galloway et al. 1983, Jeffries et al. 1979, Jeffries and Snyder 1981, Jones et al. 1983, Schofield 1977). Although pH depressions at the Biscuit Brook site were probably associated with nitrate, sulfate, and organic acids, nitrate appeared to be the anion dominating these episodes. Patterns at the other sites in this study, however, were less clear and depressions were probably associated with all acid anion forms. Multiple factors and processes influence the watershed response to acidic deposition so it is not surprising that different anions are associated, or not associated, with changes in stream chemistry. Additional factors or variables probably need to be considered to detect regional patterns rather than simple bivariate relations.

The lowest pH and ANC values were recorded at the two northeastern sites. Although the maximum change in pH and ANC during events was roughly comparable among sites, the southeastern sites typically had higher pH values during events so the maximum change in hydrogen ion concentration was about an order of magnitude lower in the Southeast than in the Northeast. The northeastern sites, as indicated in the next section, are approximately in steady-state with respect to sulfate inputs and outputs. The northeastern sites also appear to be near steady-state with respect to nitrate. One of the questions associated with acidic episodes is whether the frequency, duration, and magnitude of episodes increases as a system approaches sulfate (or nitrate) steady-state. These results might lend speculative support for this hypothesis. The two northeastern sites, near sulfate steady-state, had lower pH and ANC values than the southeastern sites.

5.5 BIOLOGICAL EFFECTS

The determination of biological effects (e.g. fish-kills) was outside the scope of the four site studies. No dramatic effects have been noted at any of the sites, but the intensity and duration of pH depressions in the two northeastern sites did approach those known to have adverse effects on early life stages of some fish species (J. Baker, personal communication). On the other hand, no pH depressions at any of the southeastern sites were of the magnitude or duration associated with such adverse effects (J. Baker, personal communication). Whether any adverse effects, indeed, occurred to any life forms at any of the sites is unknown.

5.6 BUDGETS

Because of data limitations, mass budgets were computed using flow-weighted seasonal concentrations and volumes (Section 3.5) to allow comparisons between regions. Dry deposition estimates were not included in budgets. As discussed below, however, the differences between constituent inputs and exports are roughly equal to regional estimates of dry deposition inputs for these constituents. The results (Section 4.5) also, are comparable with the more comprehensive budgets computed by the principal investigators (e.g., Murdoch 1986, Nix et al. 1986).

The mass budgets indicated the Biscuit Brook watershed was exporting base cations and sulfate. Murdoch (1986) reported estimates of dry deposition ranged from 17 to 60% of wet annual loading in the northeast with 30% as the value commonly used. There is some evidence to indicate that these values for dry deposition, however, might be too low (B. Hicks, personal communication). Applying the 60% estimate, sulfate export is still greater than import in Biscuit Brook indicating either that some other sulfate inputs exist or dry deposition is greater than 60% of wet deposition at this site. The decrease in sulfate concentrations during episodes in Biscuit Brook might indicate a possible internal source of sulfate, but better estimates of dry deposition are required to evaluate the budget.

Nitrate was near steady state in Biscuit Brook between October 1983 and September 1984. Nitrate break-through, comparable to sulfate break-through has been noted in some Adirondack systems (C. Driscoll, personal communication). Although there is a dry deposition component for nitrate, the fact that Biscuit Brook is near steady-state indicates further investigation of nitrogen dynamics is warranted.

Sulfate also is being exported at South Fork Bens Creek but dry deposition contributions of 40-50 percent of wet deposition would balance the budget. Estimates of dry deposition for the Pennsylvania region, however, are generally considered to range from 50-100 percent of wet deposition (Hicks 1984) so the Bens Creek watersheds might still be retaining some sulfate. Using bulk deposition measurements, nitrate also was near steady state in the South Fork Bens Creek watershed.

Sulfate was being retained in the southeastern watersheds. The East Fork Saline River site, however, was approaching steady state with respect to sulfate based on bulk deposition measurements. As indicated previously, the soils in the Saline watersheds are quite shallow Ultisols over extremely resistant Arkansas Novaculite bedrock. The cation and anion output from the East Fork Saline River were the lowest annual outputs recorded at any site.

The results of this study are consistent with the conclusions of Rochelle et al (1986). They used mass balance studies of sulfate to estimate annual sulfate retention (Table 5.1). Plotting the results of these studies on a map of the continental United States and southern Canada suggested that watersheds above the limit of glaciation were, in general, retaining little, if any, sulfur on an annual basis (Figure 5.4). Low annual retention of sulfur does not, however, preclude seasonal retention, which might influence the occurrence of acidic episodes.

Table 5.1. Average annual sulfate input-output budgets (SO_4-S) for sites in the U.S. and Canada (kg $ha^{-1}yr.^{-1}$) (Rochelle et al. 1986).

Watershed Location	Analytical Method	Input	Output	Retention	Percent Retention
Thompson, WA	MTB**	4.1 (B)	6.1 (L)	-2.0	--***
Eatonville, WA	MTB	8.9 (B)	6.7 (L)	2.2	25
Walker Branch, TN	MTB	14.9 (W)	11.5 (S)	3.4	23
Cross Creek, TN	MTB	14.6 (B)	10.3 (S)	4.3	29
Camp Branch, TN	MTB	11.2 (B)	9.2 (S)	2.0	19
Coweeta, NC	MTB				
WS-2		9.6 (B)	1.4 (S)	8.2	85
WS-14		12.0 (B)	1.6 (S)	10.4	87
WS-18		10.7 (B)	1.4 (S)	9.3	87
WS-32		14.6 (B)	2.5 (S)	12.1	83
WS-34		13.2 (B)	1.5 (S)	11.7	89
White Oak Run, VA	AT	10.0 (B)	6.4 (S)	3.6	36
Deep Run, VA	AT	10.0 (B)	3.3 (S)	6.7	67
Clemson, SC	IC	12.3 (B)	3.4 (L)	6.7	72
Hubbard Brook, NH	Turbid	±12.7 (B)	17.6 (S)	-4.9	--
Chesuncook, ME	IC	6.3 (B)	7.5 (S)	-1.2	--
Narragaugus, ME	IC	7.0 (W)	12.9 (S)	-5.9	--
White River, VT	IC	5.3 (W)	17.0 (S)	-11.7	--

Table 5.1. Continued.

Watershed Location	Analytical Method	Input	Output	Retention	Percent Retention
Huntington Forest, NY	IC	8.0 (W)	14.0 (L)	-6	--
Vilas County, WI	Tubrid, MTB	4.6 (B)	2.6 (L)	2.0	43
Haney, BC	MTB				
WS-A		6.1 (B)	6.7 (S)	-0.6	--
WS-C		9.7 (B)	12.2 (S)	-2.5	--
Rawson Lake, ONT	Turbid				
NW		3.7 (B)	6.2 (S)	-0.6	--
NE		3.7 (B)	1.8 (S)	1.9	51
E		3.7 (B)	3.8 (S)	-0.1	--
Harp Lake, ONT	MTB				
3		11.3 (B)	15.8 (S)	-4.5	--
3A		11.3 (B)	18.1 (S)	-6.8	--
4		11.3 (B)	15.6 (S)	-4.3	--
5		11.3 (B)	21.5 (S)	-10.2	--
Turkey Lakes, ONT	MTB				
S-31		10.2 (B)	11.9 (S)	-1.7	--
34		10.2 (B)	15.0 (S)	-4.8	--
39		10.2 (B)	13.9 (S)	-3.7	--
49		10.2 (B)	12.3 (S)	-2.1	--
Kananaskis Valley, AB	IC	6.3 (W)	17.4 (S)	-11.1	--
Jamieson Creek, BC	Spec. T.	6.7 (B)	9.0 (S)	2.3	--
Vancouver Island, BC	Turbid	8.7 (B)	28.2 (S)	-19.5	--

Table 5.1. Continued.

Watershed Location	Analytical Method	Input	Output	Retention	Percent Retention
Kejimkujik, NS (Lower Mersy River)	MTB	7.4 (W)	11.6 (S)	-4.2	--
Panther Lake, NY	AT	15.6 (W+D)	16.9 (S)	-1.3	--
Sagamore Lake. NY	AT	13.7 (W+D)	19.3 (S)	-5.6	--
Woods Lake, NY	AT	13.8 (W+D)	14.3 (S)	-0.5	--

** MTB = Methylthymol Blue, AT = Automated Thorin, IC = Ion Chromatograph, Turbid = Turbidimetric, $BaCl_2$, Spec. T. = Spectrophotometric Thorin.

*** (--) indicates negative sulfate retention.

± The data presented are the result of an average of all the undisturbed watersheds monitored on the Hubbard Brook Experimental Forest, 1963-1974.

(B) = bulk precipitation, (W) = wetfall, (D) = dryfall, (L) - soil leachate,
(S) = streamflow

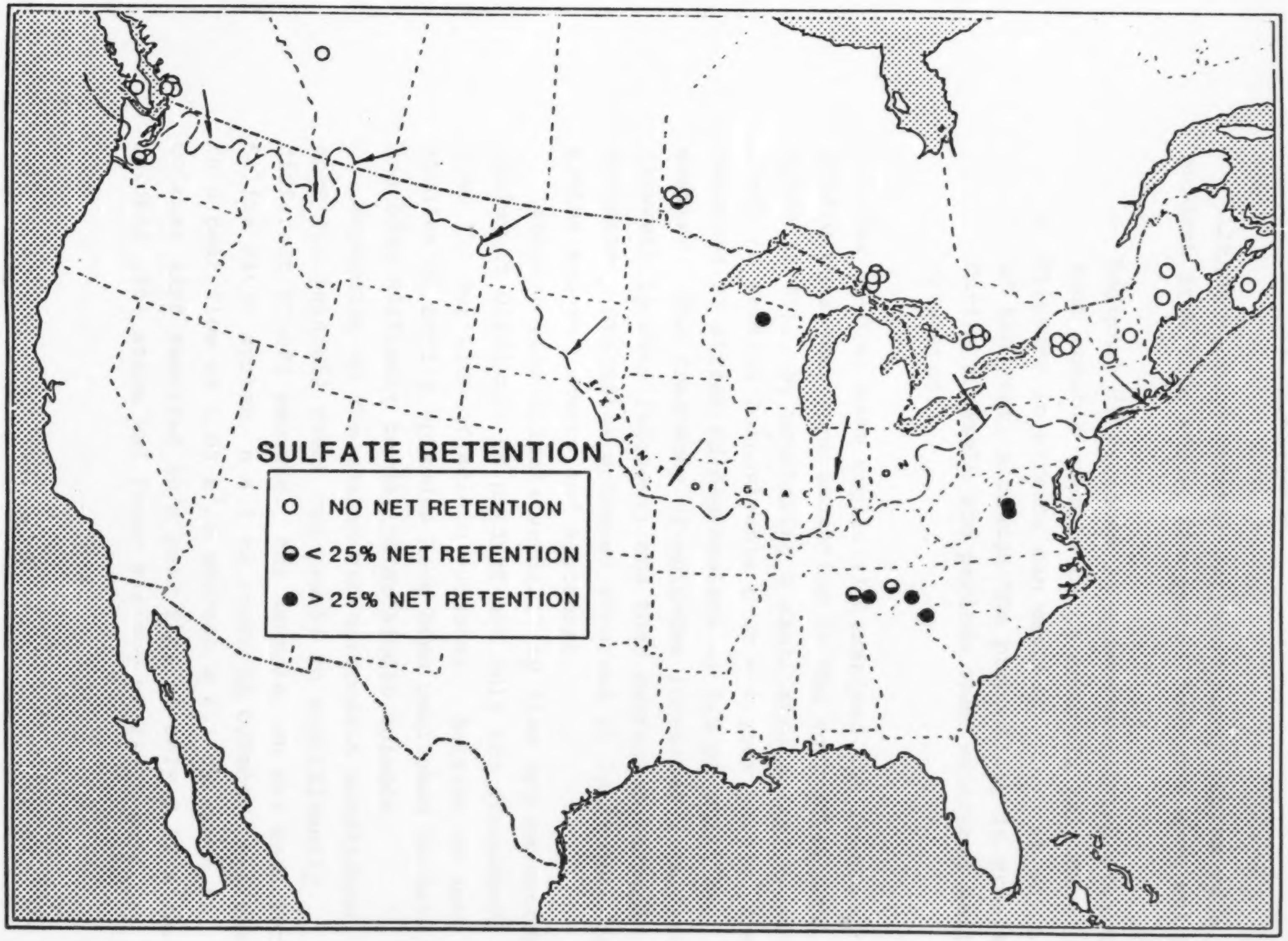
SULFATE RETENTION
○ NO NET RETENTION
◐ < 25% NET RETENTION
● > 25% NET RETENTION
EXTENT OF GLACIATION

Figure 5.4. Percent sulfate retention for the intensively studied sites in the U.S. and Canada relative to the southern extent of Wisconsinan glaciation (Rochelle et al. 1986).

5.7 FREQUENCY OF EPISODES

Although broad general patterns among storms were not evident from this study, two generalizations were evident:

- Regional differences in episodes existed with the most notable example being snowmelt episodes; and
- Episodes in streams can probably occur at any time of the year, although the probability is greater during snowmelt and periods when watershed soils are saturated.

Few studies have explicitly examined the frequency of acidic episodes. One exception is the work of Corbett and Lynch (1985). By monitoring a small stream (123 ha watershed) in central Pennsylvania over a 4 year period, they recorded 33 stream pH depressions of 0.3 pH units or greater. The frequency of episodes increased from January (lowest) to June (highest) and then decreased through December. Stormflow episodes occurred at least once for all months except January and September.

Year-to-year climate variability also can be extreme, making it difficult to predict not only the frequency, but also the duration of acidic episodes. Because no long term studies of acidic episodes have been published to date, it has been difficult to define an acidic episode.

Depending on the season and antecedent conditions, a specific rainfall event can result in significantly different runoff amounts. For example, on the East Fork Saline River system, a 4.2 cm storm in October 1984 resulted in a peak flow of 1.02 m^3/s whereas a 4.1 cm storm in October 1985 resulted in a peak flow of only 0.12 m^3/s. The October 1984 storm had lower minimum pH (6.16 vs 6.66) whereas the October 1985 storm had a larger ANC depression (76.3 vs 15 ueq/l).

Because it is desirable to be able to define an episode, several techniques (e.g., Hall 1968) were investigated to separate baseflow from storms and thereby define an episode. There were insufficient data available on the study watersheds to make definitive comparisons between regions.

There was one approach, however, that might have potential for comparing episodes regionally. The approach is to determine the average runoff from a 1 year 24 hour duration rainfall event. A 1 year 24 hour duration event is a 24 hr rainfall event that has a probability of occurring once per year. The selection of the 1 year 24 hour event is strictly arbitrary. It could have been a 6 month 12 hour event or a 2 year 24 hour event. For this example, the precipitation amounts for a 1 year 24 hour event were obtained from NWS (1961) and multiplied by the average percent runoff for the region. Multiplying this runoff by the drainage area and dividing by the number of seconds in 24 hours yields a mean daily flow.

The results are:

Basin	1 yr 24 hr Precip, cm	Avg Runoff	Runoff cm	Flow m^3/s
Biscuit Brook	7.6	0.60	4.6	5.24
S. Fork Bens Creek	5.8	0.45	2.6	2.60
Moses Creek	8.9	0.48	4.3	5.50
Jarrett Creek	8.9	0.48	4.3	3.85
East Fork Saline	8.9	0.56	5.0	3.62

The flow of 5.24 m^3/s at Biscuit Brook is near the arbitrary base value of 5.66 m^3/s (200 cfs) that the U.S. Geological Survey has established for that basin to identify peak discharges for inclusion in a partial duration frequency analysis. During water year 1984, there were 5 events that exceeded a peak flow of 5.66 m^3/s in Biscuit Brook. Although not all of these events were sampled, the events that were sampled exhibited significant surface water acidification (Table 4.11). This observation also was true for storms in the other study basins. These basins also had peak discharges greater than the flows in the above table. In general, one would expect these comparative peak discharges to be exceeded at least once per year. Therefore, the probability that an event will occur in a given geographic region can be estimated.

The effect of the episode on stream resources also will be influenced by the duration of the episode. The duration of an elevated flow event is not the same as the duration of a rainfall event. Duration generally is a function both of the type of event and watershed size or drainage area. Snowmelt episodes, for example, have durations that might be from 4-10 times longer than storm event durations. Snowmelt episodes in North Fork Bens Creek had durations of 160 hr or greater whereas the duration of some storm events was 24 hr or less.

Watershed size or drainage area also influences the duration of events. There is an apparent compensation point with watershed size where the increased duration of larger storms associated with larger basins is compensated by increased dilution of acidic inputs and the potential for increased neutralization in the watershed.

5.8 DISCHARGE-CONCENTRATION RELATIONS

General discharge-constituent relations among all sites such as decreased pH with increased discharge were not identified in this study. Murdoch (1986), however, did identify several constituent-discharge relations in Biscuit Brook that accounted for over 50 percent of the constituent variability as a function of discharge. Many factors such as antecedent conditions, differential loading on the hydrograph, drainage area, seasonal biotic differences and small sample size combine to confound the identification and detection of underlying episodic patterns. Two of these factors, differential hydrograph loading or hysteresis and drainage area influences, will be illustrated using data from the East Fork Saline River.

Various constituents load differently on the rising and falling limbs of the hydrograph. This complicates the development of general discharge-concentration relationships. For example, during one storm in the East Fork Saline River watershed, sodium loaded rapidly during the initial runoff period (Figure 5.5). As the storm progressed, the loading rate decreased and became relatively uniform on the remaining portion of the rising limb. When the rainfall stopped, the loading rate decreased on the falling limb. Sodium loading exhibited three different discharge-concentration relations during this December storm. These different relations are indicated by the clockwise trace of the sodium-discharge relation in Figure 5.5. The general pattern and actual cation load varied both among storms and among seasons so no general discharge-concentration relation could be developed.

Watershed size or drainage area also influences the stream response. An additional station (Campsite Station) for baseflow monitoring was established on the East Fork Saline River. The watershed area above the Campsite Station was 2.8 km^2 compared to 2.1 km^2 for the North Fork Saline River (another tributary that was sampled by Nix et al. 1986) and 6.3 km^2 for the entire East Fork Saline drainage basin. The biweekly pH and ANC measurements for these three stations are shown in Figures 5.6 and 5.7, respectively. Stream chemistry at the Campsite and North Fork Stations were nearly identical throughout the year with significantly

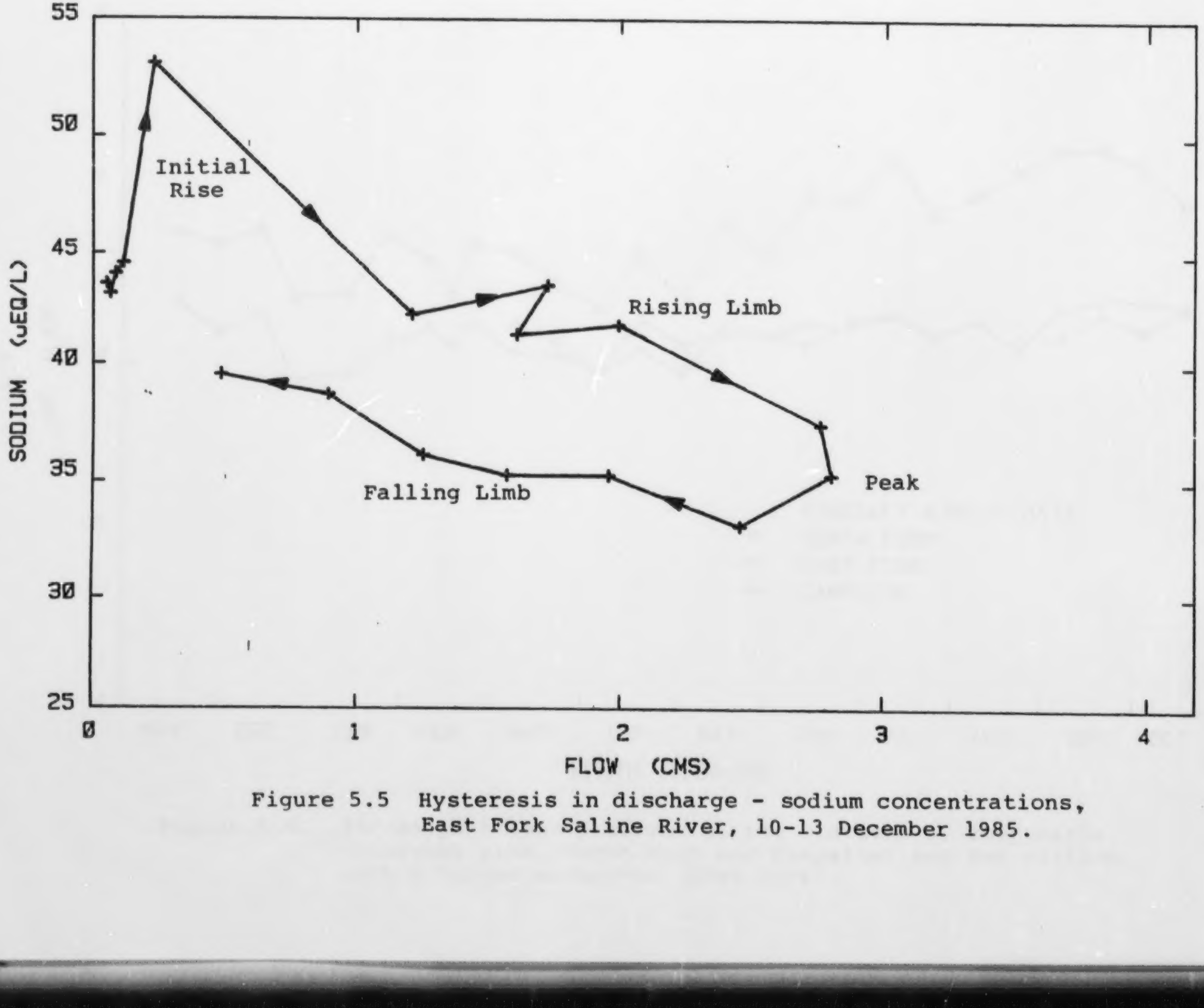

Figure 5.5 Hysteresis in discharge - sodium concentrations, East Fork Saline River, 10-13 December 1985.

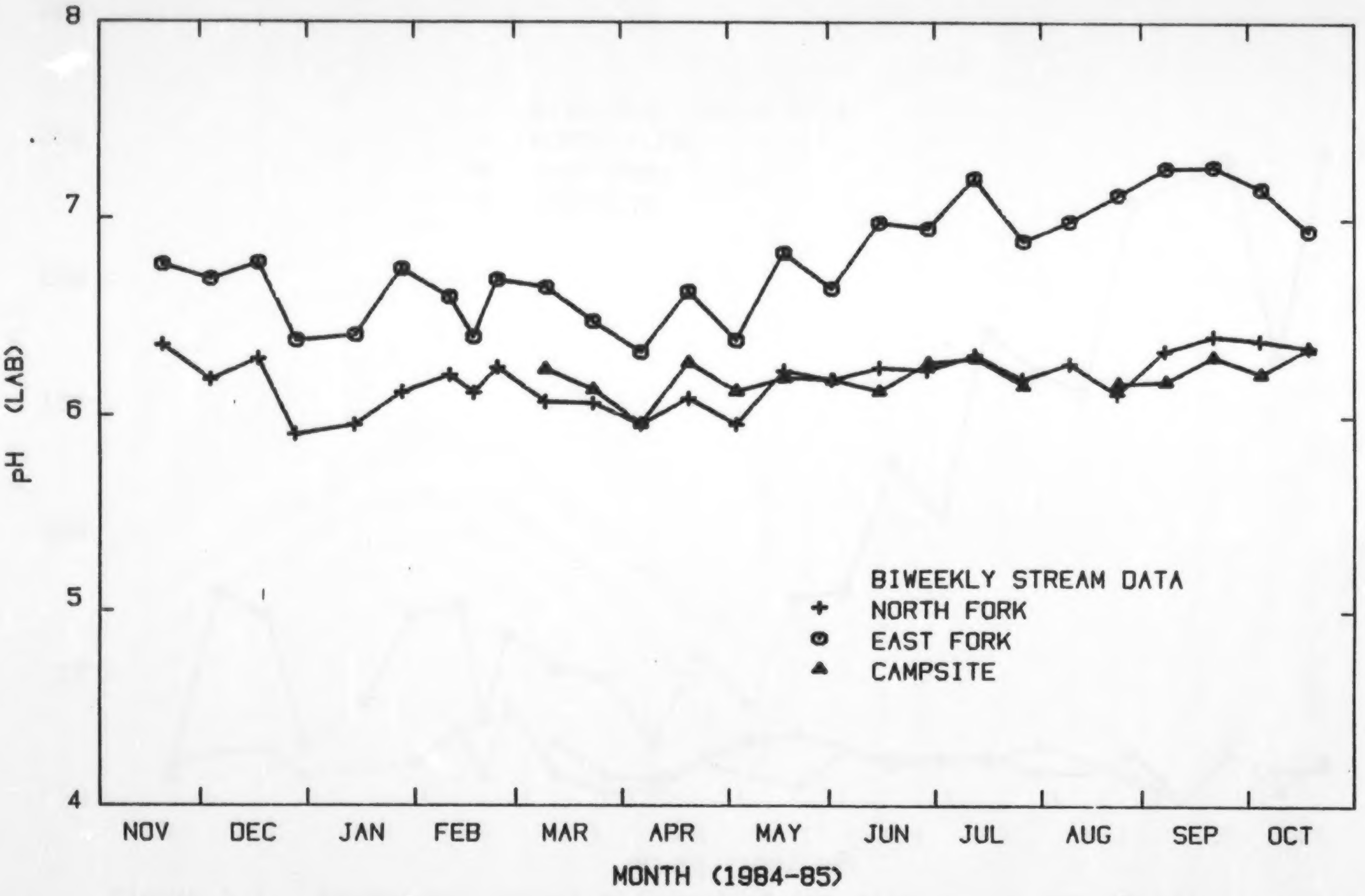

Figure 5.6. Stream pH values observed at two stations of comparable watershed size (North Fork and Campsite) and one station with a larger watershed (East Fork).

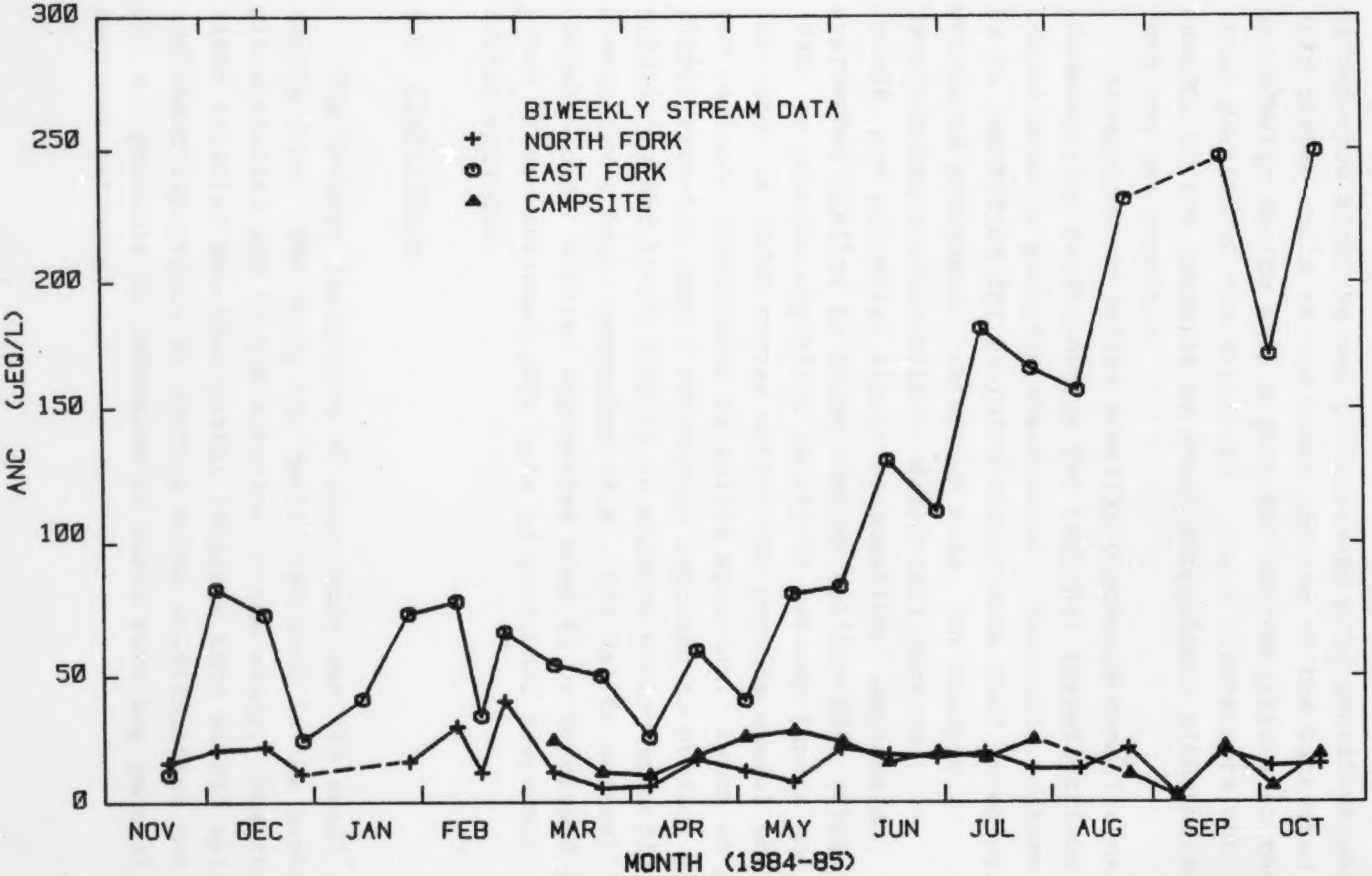

Figure 5.7. Stream ANC values observed at two stations of comparable watershed size (North Fork and Campsite) and one station with a larger watershed (East Fork).

lower pH and ANC values than in the East Fork. These differences might be due to increased pCO_2 contributions from deeper soils in the lower portion of the watershed or a groundwater source with higher ANC concentrations in the lower portion of the watershed. Storm events were not sampled at the Campsite so event comparisons with the North Fork are not possible.

Attempting to define specific discharge-constituent concentration relationships for regional investigations or comparisons is probably unwarranted. Surrogate factors need to be identified for regional comparisons that integrate watershed processes. Watershed area, for example, incorporates considerations of rainfall interception, runoff, and potential discharge duration. Regression approaches similar to those used by Vollenweider (1968, 1975) to provide empirical relations between inputs and an indicator or index system output can provide useful tools for regional comparisons of acidic episodes. Lynch et al. (1986) recently used a regression approach to predict pH, alkalinity and total acidity in streams during episodic events for a small watershed (i.e., 123 ha) in central Pennsylvania. Similar approaches need to be developed for a broad cross-sectional data base of watershed responses during episodes.

5.9 LIMITATIONS

The primary limitation of this study was the small sample size. The study was restricted both in the number of sites studied and in the duration of the study. The four sites selected provided useful insights into acidic episodes and their importance in surface water acidification but it was not possible to determine if there were any general regional patterns.

The study duration also was a severe restriction. The hydrologic data generally were available for only one year. The general relation of precipitation in the study year to the historical precipitation data (Figure 2.2) is shown in Table 5.2. It is apparent there were regional differences in the seasonal and annual precipitation patterns. The hydrologic response of the watersheds in other years, however, is unknown. It is difficult to interpret and compare stream chemistry from two different types of hydrologic years at different sites such as a wet year at one site and a dry year at another site. Future studies should investigate multiple sites for multiple years using complete, comprehensive procedures for data collection.

Table 5.2. Relation of site study year precipitation to historical precipitation.

Site	Annual	Winter	Spring	Summer	Fall
Biscuit Brook	A-W	W	A-W	A	D
S. Fork Bens Creek	W	W	W	W	A
Jarrett, Moses Creeks	W	W	W	W	A
East Fork Saline	A-W	A-W	A	A-D	A

A = average

W = wet

D = dry

6.0 SUMMARY AND CONCLUSIONS

Although specific patterns and criteria for episodes were not identified, five general conclusions were evident:

- o Regional differences in precipitation, stream, and episodic stream chemistry exist;
- o Episodes of alkalinity and pH depressions can occur at any time of the year but the probability of occurrence is greater during snowmelt and periods when watershed soils are saturated;
- o Snowmelt was the dominant episodic period both in magnitude and duration of acidic inputs;
- o Although nitrate appeared to be the dominant anion during episodes at the Biscuit Brook site, other acid anions could be important at this site and it is likely that all acid anions contribute to pH depressions at the other sites studied; and
- o Developing a protocol and procedures for estimating the probability that episodes will occur is feasible.

The study sites were originally selected by the principal investigators (Murdoch, Olem, Witt and Barker, and Nix and Thornton) to be typical of the geographic region in which they were located. The study sites all had similar sized drainage basins. The streams were between 4.0 and 6.0 m in width with water depths generally less than 0.5 m. All the streams maintained continuous streamflow throughout the year and all supported a sport fisheries (e.g. trout or smallmouth bass).

Each site was receiving acid deposition. The volume weighted pH values for wet deposition ranged from 3.89 to 4.92. Generally, minimum pH values and maximum sulfate concentrations occurred in the summer.

The baseflow pH values at the northeastern sites were more acidic (flow weighted seasonal average 5.2 to 6.4) than the southeastern sites (flow weighted seasonal average 6.5 to 7.3). Annual average flow weighted total base cations at the southeastern sites (133 to 178 ueq/l) were less than at the northeastern sites (192 to 314 ueq/l). Calcium was the primary cation responsible for these differences. In the northeastern sites, calcium was the dominant base cation and had concentrations two to three times greater than the calcium concentrations in the southeastern sites. In the southeastern streams sodium generally was the dominant base cation. Watershed geology and weathering products were related to the dominant cations in the streams. Annual average flow weighted sulfate and nitrate concentrations at the northeastern sites were about an order of magnitude higher than the southeastern streams.

The following patterns in stream chemistry were identified based on seasonal flow-weighted values. Minimum baseflow pH values generally occurred in the winter and/or spring (i.e., during snowmelt) at each of the study sites. Both minimum baseflow sulfate and ANC occurred in the spring. Maximum average sulfate concentrations occurred predominantly in the fall, although the sites located in the Southern Blue Ridge Province had maximum average sulfate concentrations in the summer. Minimum average nitrate concentrations occurred in the summer and fall and the maximum nitrate concentrations occurred predominantly in the winter.

ANC concentrations and pH values decreased during all storm events at all sites. Based on mean storm event concentrations, calcium decreased during the majority of the events and dissolved aluminum increased during all events. At the northeastern sites, sulfate concentrations generally decreased during episodes whereas in the southeast sulfate concentrations increased during events. Although mean event nitrate concentrations decreased at the East Fork Saline River and North and South Fork Bens Creek, nitrate concentrations increased at the other sites. At the northeastern sites and at the East Fork Saline River site, chloride decreased during events, but chloride concentrations increased in the Southern Blue Ridge Province sites.

Although pH depressions at the two northeastern sites approached intensities and durations associated with adverse effects on fish species, these stream sites currently support fish and no such adverse effects have been observed. At none of the southeastern sites did pH depressions occur at a magnitude or duration associated with adverse effects on fish.

Mass budget calculations based on wet deposition only showed that hydrogen ions were being retained at all sites. There was a net export of sulfate at the Biscuit Brook and South Fork Bens Creek sites whereas the southeast sites were retaining sulfate. Assuming our estimates for dry deposition are reasonable, the northeast sites are at steady state with respect to sulfate inputs and outputs. The East Fork Saline River site also appears to be approaching steady state with respect to sulfate (Section 5.5). Biscuit Brook and South Fork Bens Creek were near steady state with respect to nitrate for the 1984 budget period. During 1984, Biscuit Brook retained about 11 percent of nitrate inputs and South Fork Bens Creek retained about 14 percent. All the other sites were retaining greater than 90% of the nitrate (Table 4.14).

Because episodes are driven by hydrometeorological events, a better understanding of the interaction among hydrometeorological and other watershed processes such as cation supply and mobile anions is necessary. Also, comparisons among sites and regimes should be based on similar hydrologic seasons and types of events and not on calender seasons. For example, the low flow season in the Laurel Hill area occurs from July through October but in the Southern Blue Ridge Province it occurs later in the year and is of shorter duration (i.e., September through November). The type of event also influences the occurrence of episodes (e.g., snowmelt events initiated by rainfall versus rainfall or storm events).

Developing criteria and a protocol for estimating the probability that episodes will occur is feasible. The probability of episodes appears to be related to the seasonal/annual probabilities that elevated flow events will occur.

Although regression or other empirical approaches provide a vehicle for making regional comparisons, multiple sites within regions, multiple years of hydrologic record, and complete, comprehensive site records are required to evaluate the episodic acidification of streams.

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APPENDIX A
STAGE-DISCHARGE CALCULATIONS
JARRETT AND MOSES CREEKS

APPENDIX A

Daily flows for Jarrett and Moses Creeks in North Carolina were not available in Olem (1986). In order to utilize the available stage records, stage-discharge rating curves were developed for each stream. Because no discharge measurements were taken, rating curves were developed by the following procedures:

1) The following basin characteristics were computed from topographic maps and by using the Synder Unit Hydrograph procedures:

	Moses	Jarrett
Area (sq mi)	4.32	3.01
Length (mi)	4.05	2.55
Length to Centroid (mi)	2.16	1.39
Fall (ft)	2860	1790
Rainfall Duration (hrs)	0.66	0.51
Time to peak (hrs)	3.6	2.8
Length of Unit Graph Base (days)	3.5	3.3
Unit Graph Peak Discharge (cfs)	455	597

2) Peak Discharges for a 2-year rainfall event were computed from data given in Jackson (1976) and correlated with a rainfall total from TP-40 (NWS 1961) of approximately 1.25 inches. The peak discharges were 374 cfs for Moses and 290 cfs for Jarrett.

3) Based on location and soil type, SCS runoff curve NO. 70 was considered the most representative for both basins (SCS 1972).

4) Hourly rainfall data for 3 selected storms on each basin were input to the DABRO model (Golding 1982) along with required parameters of area, time to peak, maximum

discharge, SCS runoff curve number and time interval and the resulting discharges were plotted with the measured stages and adjusted for base flows. This process was repeated, adjusting the peak discharge and time to peak as required to produce a reasonable correlation between stage and discharge for each site. The final peak discharges and time to peak were:

	Moses	Jarrett
Unit Graph Peak Discharge (cfs)	350	340
Time to Peak (hrs)	3.0	2.8

5) Hourly discharges were computed by applying observed stages to the rating curves. For periods of missing stage records, discharges were estimated by drainage area ratio method from the station with available data and by inspection of rainfall data if available.

6) Daily discharges were then computed, as were daily runoff and monthly runoff in inches. These data were then compared with USGS data at two sites in the vicinity for the study period (May 1984 - March 1985):

	Runoff (inches)	Precipitation (inches)	Runoff Ratio
Moses Creek	39.7	45.7	0.87
Jarrett Creek	44.8	57.2	0.78
Nanatahala River	25.4	34.2	0.74
Pigeon River	25.7	35.3	0.73

The higher runoff ratios for Moses and Jarrett Creeks are expected because their drainage areas are smaller than the Nanatahala (51.9 mi^2) and Pigeon (27.6 mi^2) Rivers.

APPENDIX B

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK MONITORING STATIONS USED TO DETERMINE REGIONAL CONSTITUENT CONCENTRATIONS

APPENDIX B

Region I
(Biscuit Brook)

Station Number	Location
220815	Quabbin Reservoir, Hampshire County, MA Longitude: 72 23 27 Latitude: 42 21 40
470100	Bennington, Bennington County, VT Longitude: 73 09 48 Latitude: 42 52 34
397220	Milford, Pike County, PA Longitude: 74 49 13 Latitude: 41 19 39
336500	Jasper, Steuben County, NY Longitude: 77 32 08 Latitude: 42 06 22
335240	Bennett Bridge, Oswego County, NY Longitude: 75 56 50 Latitude: 43 31 34
335141	West point, Orange County, NY Longitude: 74 02 54 Latitude: 41 21 03
332020	Huntington Wildlife, Essex County, NY Longitude: 74 13 25 Latitude: 43 58 19
330860	Aurora Research Farm, Cayuga County, NY Longitude: 76 39 35 Latitude: 42 44 02
312981	Washington Crossing, Mercer County, NJ Longitude: 74 51 17 Latitude: 40 18 54
336840	Biscuit Brook, Ulster County, NY Longitude: 74 30 13 Latitude: 41 59 39

Region II
(Laurel Hill)

Station Number	Location
210360	White Rock, Carroll County, MD Longitude: 76 59 42 Latitude: 39 24 04
367160	Wooster, Wayne County, OH Longitude: 81 55 31 Latitude: 40 46 48
364900	Caldwell, Noble County, OH Longitude: 81 31 52 Latitude: 39 47 34
501860	Parsons, Tucker County, WV Longitude: 79 39 44 Latitude: 39 05 23
482890	Shenandoah National Park-Big Meadows, Madison County, VA Longitude: 78 25 45 Latitude: 38 30 51
394200	Leading Ridge, Huntington County, PA Longitude: 77 56 10 Latitude: 40 39 32
392940	Kane Experimental Forest, Elk County, PA Longitude: 78 46 04 Latitude: 41 35 52
391520	Penn State, Centre County, PA Longitude: 77 56 47 Latitude: 40 47 18
331000	Chautauqua, Chautauqua County, NY Longitude: 79 23 47 Latitude: 42 17 58

Region III (Southern Blue Ridge Province)

Station Number	Location
441190	Great Smokey Mountains National Park-Elkmont, Sevier County, TN Longitude: 83 35 25 Latitude: 35 39 52
11020	Sand Mountain Experiment Station, DeKalb County, AL Longitude: 85 57 32 Latitude: 34 17 30
441140	Giles County, Giles County, TN Longitude: 86 54 12 Latitude: 35 17 05
342500	Coweeta, Macon County, NC Longitude: 83 25 50 Latitude: 35 03 38
440040	Walker Branch Watershed, Anderson County, TN Longitude: 84 17 14 Latitude: 35 57 41
421880	Clemson, Pickens County, SC Longitude: 82 50 09 Latitude: 34 40 28
343460	Piedmont Research Station, Rowan County, NC Longitude: 80 37 22 Latitude: 35 41 48
182260	Lilley Cornett Woods, Letcher County, KY Longitude: 82 59 37 Latitude: 37 04 40
114140	Georgia Station, Pike County, GA Longitude: 84 24 22 Latitude: 33 10 40

Region IV
(Ouachita Mountains)

Station Number	Location
40380	Caddo Valley, Clark County, AR Longitude: 95 05 55 Latitude: 34 10 46
42700	Fayetteville, Washington County, AR Longitude: 94 10 24 Latitude: 36 06 02
41620	Buffalo National River, Marion County, AR Longitude: 92 32 58 Latitude: 36 05 20
40260	Warren 2WSW, Bradley County, AR Longitude: 92 06 02 Latitude: 33 36 15
190620	Hill Farm Research Station, Claiborne County, LA Longitude: 93 03 02 Latitude: 32 45 04
372580	Clayton Lake, Pushmataha County, OK Longitude: 95 21 10 Latitude: 34 31 42
452180	Longview, Gregg County, TX Longitude: 94 42 49 Latitude: 32 22 53
453800	Forest Seed Center, Nacogdoches County, TX Longitude: 94 51 39 Latitude: 31 33 38